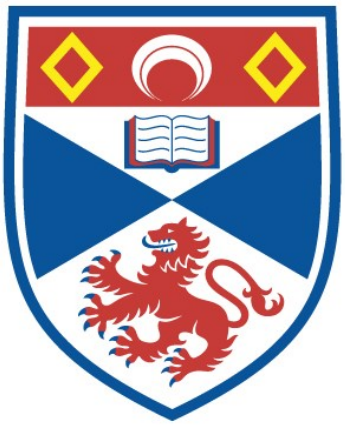
TRIPHENYL AND TETRAPHENYL CYCLOPENTADIENYLIDES

Michael Inglis Campbell Singer

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1968

TRIPHENYL- AND TETRAPHENYL-

CYCLOPENTADIENYLIDES

being a Thesis

presented by

MICHAEL INGLIS CAMPBELL SINGER, B.Sc.,

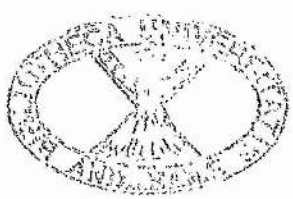
to the

UNIVERSITY OF ST. ANDREWS

in application for

THE DEGREE OF DOCTOR OF PHILOSOPHY

St. Andrews August, 1968



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DECLARATION

I declare that this thesis is based on the results of experiments carried out by me, that it is my own composition and has not previously been presented for a Higher Degree.

The work was carried out in the Department of Chemistry of the United College in the University of St. Andrews, under the direction of Mr. D.M.G. Lloyd, B.Sc., F.R.I.C.

CERTIFICATE

I hereby certify that Mr. Michael Inglis Campbell Singer, B.Sc., A.R.I.C., has spent eleven terms at research work under my supervision, has fulfilled the conditions of Ordinance No, 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Ph.D.

Director of Research.

UNIVERSITY CAREER

I entered the University of St. Andrews as an undergraduate in October 1961 and graduated B.Sc. with Second Class Honours in Chemistry in July, 1965.

The research described in this thesis was carried out between October 1965 and July 1968, during which time I held a Research Studentship awarded by the University of St. Andrews.

PUBLICATIONS

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(3) Ylides and Phosphazines from Diazocyclopentadienes in Molten Triphenylphosphine.
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(4) An Arsonium Ylide from a Carbene and an Arsine.
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(8) $p\pi$-$d\pi$ Orbital Interactions in Heteronium Ylides.
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(9) A New Route to Arsonium Ylides.
Harris, G.S., Lloyd, D., Preston, N.W. and Singer, M.I.C., Chem.and Ind., in press

ACKNOWLEDGEMENTS

I wish to thank Mr. Douglas Lloyd for providing this topic of research and for his readily available advice and encouragement throughout the last three years.

I am indebted to the many members of the Chemistry Department who have cheerfully given assistance and suggestions, and in particular my thanks are due to Dr. G.S. Harris and Dr. F. Inglis for their personal interest in this work and for gifts of triphenylstibine, triphenylbismuth, and triphenylarsine oxide.

I am also grateful to Nicky who helped type this thesis for her patience and understanding.

Finally I gratefully acknowledge a Research Studentship from the University of St. Andrews.

SUMMARY

The thermal decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in pyridine and methyl pyridines has been found to provide a route to the corresponding pyridinium 2,3,4,5-tetraphenylcyclopentadienylide. This procedure has been extended to include decomposition of the diazo compound in derivatives of Group V and VI elements and a route to a series of hitherto unreported tetraphenylcyclopentadienylides has been established. Triphenylphosphonium, triphenylarsonium, and triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylides have been isolated as stable crystalline solids and evidence has been found for the existence of the triphenylbismuthonium analogue. Diphenylsulphonium, methylphenylsulphonium, and diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylides have also been shown to have unusual stability.

The mechanism of the decomposition reaction of 2,3,4,5-tetraphenyldiazocyclopentadiene is discussed and is considered to proceed by initial decomposition of the diazo compound to tetraphenylcarbenacyclopentadiene followed by electrophilic attack on a suitable hetero-atom group containing a lone pair of electrons.

A comparative study of the properties and the reactivities of the tetraphenylcyclopentadienylides with carbonyl compounds and nitrosobenzene has been made. The pK_a's of some of the

ylide conjugate acids were determined in 95% ethanol solution and it appears that for the similarly substituted ylides there is no consistent parallel between nucleophilicity and basicity.

The thermal decomposition of other diazocyclopentadienes, including the 2,3,4,5-tetrachloro-, 2,3,4-triphenyl-, 5-bromo-2,3,4-triphenyl-, and 5-chloro-2,3,4-triphenyl- derivatives, occurred uncontrollably and attempts to obtain ylides failed when these diazo compounds were subjected to analogous conditions employed for 2,3,4,5-tetraphenyldiazocyclopentadiene.

Phosphines were found to couple readily with substituted diazocyclopentadienes to form the corresponding phosphazines with the exception of the reaction between triphenylphosphine and 2,3,4,5-tetraphenyldiazocyclopentadiene. Evidence suggests that these phosphazines, in acidic media, are protonated at the nitrogen atom rather than at the five-membered ring.

Pyridinium 2,3,4-triphenylcyclopentadienylide was prepared by alkylation of pyridine with 5-bromo-2,3,4-triphenylcyclopentadiene in a solution of nitromethane and subsequent basification. In an attempt to prepare the analogous phosphonium ylide it was found that triphenylphosphine in nitromethane led to reduction of the bromo compound. However when this reaction was carried out in the absence of solvent triphenyl-(2,3,4-triphenylcyclopentadienyl)phosphonium bromide was isolated.

It has been found that triphenylarsine oxide and 2,3,4-triphenylcyclopentadiene undergo a reaction in triethylamine and phosphorus pentoxide to form triphenylarsonium 2,3,4-triphenylcyclopentadienylide, and that when the reaction is carried out in acetic anhydride the 5-acetyl ylide is formed. Some electrophilic substitution reactions on the triphenylphosphonium and triphenylarsonium 2,3,4-triphenylcyclopentadienylides have been done and the properties and nucleophilicity of these ylides have been investigated. A comparison has also been drawn between these ylides and their tetraphenylcyclopentadienylide analogues.

CONTENTS

PART III

EXPERIMENTAL

PART I

INTRODUCTION

1. NON-BENZENOID AROMATIC COMPOUNDS

During the middle of the last century it was recognised that benzene and a number of related compounds had distinctive properties and these compounds had come to be called 'aromatic'. In 1865, Kekulé proposed the cyclic structural formula for benzene[1].

The use of the word 'aromatic' was based on structural features; namely the presence of a benzene ring in a molecule. Shortly afterwards however it was suggested[2] that the concept of aromaticity should include compounds of similar chemical behaviour rather than those with a common structural feature. By the nineteen-twenties the chemical behaviour of aromatic molecules was expressed in terms of the electronic theories of chemistry being developed by Ingold[3] and Robinson[4].

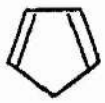
Huckel, one of the pioneers of the π-electron theory of aromaticity in terms of the simple molecular orbital theory, introduced in 1931 the basic rule underlying present day ideas on aromaticity[5]. It states that "amongst fully conjugated, planar, monocyclic olefins only those possessing $(4n + 2)$ π-electrons, where n is an integer, will have special aromatic stability". This rule embraced Robinson's concept of the aromatic sextet[4,6] of electrons and also included many other possible systems of electrons which could endow molecules with aromatic character. At the time of this

prediction no examples of these other types were known but since 1957 the preparation and isolation of many such compounds has provided excellent evidence for the validity of the rule.

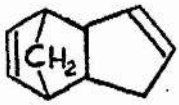
In Hückel's molecular orbital treatment the π-electrons of the conjugated system are regarded as common to all the carbon molecular orbitals. The orbitals may be bonding orbitals, non-bonding orbitals, and anti-bonding orbitals, the numbers of each of these and their energies depending on the number of atoms and the symmetry in the particular conjugated system. They may be determined by solving the wave equation for the system, not more than two electrons being allocated to each orbital in accordance with the Pauli Exclusion Principle.

Hückel's rule specifies the conditions under which five- and seven-membered carbocyclic ring compounds can possess aromatic character. Thus, cyclopentadiene (I) is formally analogous to the heterocyclic aromatic systems furan, thiophene, and pyrrole, but unlike these it is completely devoid of aromatic character. Due to the enhanced unsaturated nature of the conjugated diene system because of ring strain, the pure monomer (I) undergoes a rapid Diels-Alder reaction with itself at room temperature to form

Plate 1



I



II

III

IV

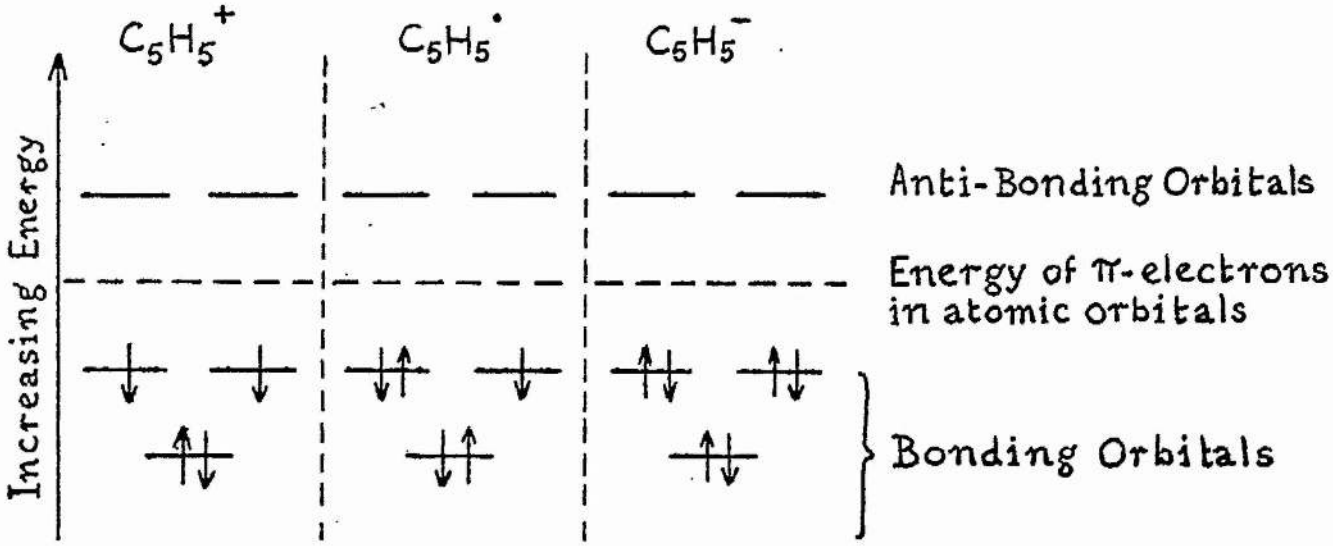


Fig. 1.1

V

VI

dicyclopentadiene(II). The heterocyclic analogues derive their aromaticity from the sextet of π-electrons composed of one unshared pair of electrons from the hetero-atom together with the four π-electrons from the double bonds. The removal of a hydrogen atom together with two, one, or none of its bonding electrons from cyclopentadiene will result in a cation $C_5H_5^+$, a radical $C_5H_5^{\bullet}$, and an anion $C_5H_5^-$ respectively. The diagram (Fig. 1.1) represents the occupancy of the molecular orbitals by the π-electrons for each of the three species. The cyclopentadienide anion (III) alone has a closed six π-electron shell and therefore the aromaticity which the parent hydrocarbon lacks. The electrons all occupy bonding orbitals (i.e. the removal of an electron requires energy expenditure) and there are no unfilled bonding orbitals (i.e. addition of an electron requires energy expenditure). This corresponds to the ground state of benzene which may be likened to the especially stable electron shells of the inert gases. The structure (III) is in fact completely symmetrical being only one of five canonical forms. The more usual representation (IV) is adopted in this thesis.

Molecular orbital calculations were also successfully applied to cycloheptatriene (V) in which it was found to have

Plate 2

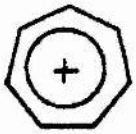
$n = 0$
2π

VII

X

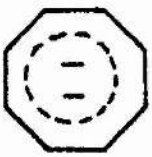
$n = 1$
6π

IV

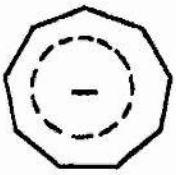


VI

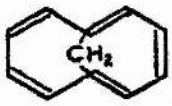
$n = 2$
10π



VIII

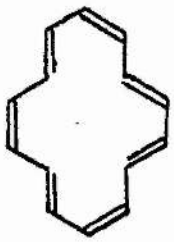


IX



XI

$n = 3$
14π



XII

three bonding and four anti-bonding orbitals. Thus of the cation $C_7H_7^+$, the radical $C_7H_7^{\bullet}$, and the anion $C_7H_7^-$, only the cation has a closed six π-electron shell. In formulating his rule Hückel predicted that cycloheptatrienylium salts, derived from (V), would have aromatic character. This prediction was fulfilled in 1954 when Doering[7] identified tropylium bromide (VI), a compound which had been prepared in 1891[8] but was not identified.

The two carbocyclic systems discussed so far are examples in which the number of π-electrons is $(4n+2)$ where $n=1$. Hückel's rule forecast new non-benzenoid aromatic systems in which the number of π-electrons in a closed shell could be 2 or 10 or 14 etc.. Until 1957 no such monocyclic systems were known but in that year Breslow[9] prepared the cyclopropenium salt (VII) in which 2 π-electrons are delocalised over three ring atoms. This discovery was the first of many new aromatic monocyclic systems, such as the cyclooctatetraenide dianion[10] (VIII) and the cyclononatetraenide anion[11] (IX) both of which have a closed shell of ten π-electrons. It has also been reported that the cyclobutadiene di-cation (X) has been obtained in solution,[12] this being another example of a monocyclic system containing two delocalised π-electrons. Sondheimer has prepared a series of completely conjugated polyolefins

known as annulenes[13] (e.g. [14] -annulene (XII)) and studies of these compounds, especially their nuclear magnetic resonance spectra, have given added support to Hückel's rule. Similarly the bridged annulenes[14], of which (XI) is an example, confirm the prediction which Hückel made in 1931. It is theoretically possible on the basis of Hückel's rule that aromatic systems containing a large number of π-electrons can exist. However the existence of such macrocyclic systems in the form of plane regular polygons is unlikely owing to the great angular strain, and the transition of the molecules into a non-planar form would considerably diminish the conjugated energy. Another possible reason for lack of aromaticity in larger rings arises from the suggestion that above a certain ring size, alternating single and double bonds may be expected rather than hybridised bonds [15]. In general the delocalisation energy per double bond in annulenes decreases as the ring size increases.

Breslow and Yuan [16] have restated Hückel's rule to accommodate both the uncharged planar cyclic polyolefins and the aromatic ions such as the tropylium, cyclopentadienide and cyclopropenium ions. It states that: "The π-electron molecular orbitals of monocyclic conjugated molecules vary with the number of carbon atoms such that $(4n+2)$ numbers of

electrons completely fill the bonding molecular orbitals and produce the largest electron delocalisation energy. (4n+1) and (4n+3) electron molecules (radicals) tend to form a 'more stable' system through the gain or loss of an electron to form the (4n+2) configuration".

Aromatic Derivatives of Cyclopentadiene.

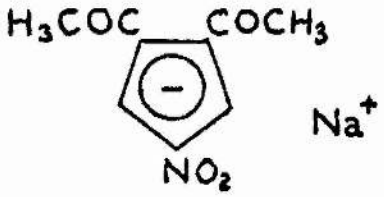
Cyclopentadiene, with a pK_a of 15[17], is more acidic than other hydrocarbons apart from the acetylenes. (cf. triphenylmethane, pK_a = 33). The related compounds indene and fluorene have pK_a's of 18.5 and 23 respectively. The acidity of cyclopentadiene is associated with the aromaticity of the ion (IV). Thiele recognised this acidity when he prepared the first cyclopentadienide anion[18] by the action of potassium on cyclopentadiene in an inert atmosphere and solvent. The anion has recently been prepared more satisfactorily by the action of phenyl lithium on cyclopentadiene[19]. Salts have also been obtained with manganese and with alkaline-earth and rare-earth metals. These salts are highly reactive and inflame in air, but are nonetheless stable, deriving this stability from the delocalised sextet of π-electrons. The reactivity of the cyclopentadiene anion is reduced considerably if electron-withdrawing substituent groups are attached to the ring. An example of

such an anion, the diacetylnitrocyclopentadienide salt (XIII), was prepared by Hale in 1912[20], and it appears to be stable indefinitely in the atmosphere. Other such anions which can be handled in air include aroyl[21,22], formyl[23], cyano[24], and carbomethoxycyclopentadienides[25-28].

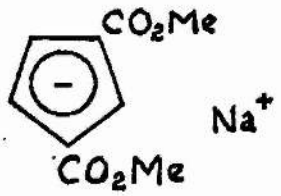
The aromatic character of the cyclopentadienide anion is shown both by its chemical reactions and by its physical properties. The anion shows a high reactivity towards electrophilic attack. With carbon dioxide the unsubstituted anion gives a dicarboxylic acid which dimerises[18,29], and with water and alcohol it is decomposed. It is aroylated by acid chlorides in the absence of catalysts to give monomeric diaroyl derivatives[21,22]. The cyclopentadienide anion undergoes ready electrophilic substitution with methyl iodide in liquid ammonia to give methylcyclopentadienes[30]. Deuterium exchange occurs readily[31] in alkaline media (cf. pyrrole which only undergoes exchange at pH<1)[32] illustrating the high reactivity of the anion.

Physical evidence for the aromatic and ionic nature of the cyclopentadienide anion is abundant. Whereas cyclopentadiene shows two multiplets in its nuclear magnetic resonance spectrum at 3.57τ and 7.13τ arising from the olefinic and methylene protons respectively[33], the nuclear magnetic resonance spectrum of sodium cyclopentadienide

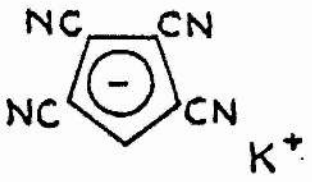
Plate 3



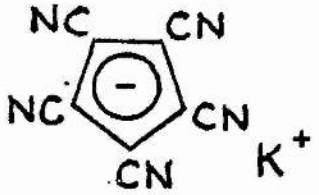
XIII



XIV



XV



XVI

shows one sharp peak at 4.5τ indicating the symmetry of the anion[33]. The position of the peak due to the protons in benzene occurs at 2.73τ. This change in positions is thought to occur because of electron density differences on the carbon atoms rather than any difference in the magnitude of the ring currents in the cyclopentadienide anion and benzene.

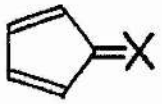
The symmetry of the anion has also been concluded from work on ^{14}C-labelled cyclopentadiene[34], in which attempts were made to produce labelled cyclopentadiene from 1,2-dibromocyclopentane labelled at the 4-position with ^{14}C. In each of the three different methods used random distribution of the ^{14}C in the resultant cyclopentadiene was found, providing strong evidence that each preparative route involved formation of the cyclopentadienide anion in which all five positions are equivalent.

Peters prepared the unreactive anion sodium dicarbomethoxy-cyclopentadienide[25](XIV) and its ionic nature is suggested by the following observations. It does not melt, it is soluble in polar solvents and insoluble in normal organic solvents. Also lead and barium salts can be formed by double decomposition, and the conductivity of its aqueous solutions indicates a 1:1 electrolyte. Webster has recently prepared the remarkably stable tetra- and pentacyanocyclopentadienide

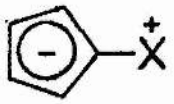
anions (XV) and (XVI)[24,35]. For instance, the potassium salt of the latter can be heated to 400° in air without decomposition. A number of electrophilic substitution reactions on the tetracyanocyclopentadienide anion have been reported, some of which have been done in strongly acid media. Normally these conditions cannot be employed with the cyclopentadienide system because of the basicity of the anion, but when the basicity of the anion is reduced by the presence of nitrile groups strongly acid conditions can be used.

If an exocyclic double bond is added to the five-membered ring (XVIIa) 6 π-electrons become available provided that polarisation in the direction indicated by (XVIIb) is possible. This will depend on the electronegativity of the atom or group X. Examples of compounds of type (XVII) in which X is an electron donating atom or group are known as cyclopentadienylides, and these compounds together with the analogous dibenzocyclopentadienylides (fluorenylides) are discussed in detail in Part I, Section 2. When X is a strongly electronegative element such as oxygen molecules less stable than the corresponding cyclopentadienes result. Cyclopentadienone itself (XVIIa; X = O) has not been isolated and it has been shown that[36] the simpler

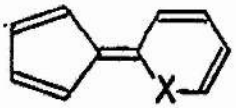
Plate 4



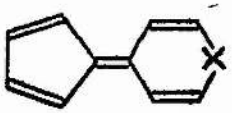
XVII a



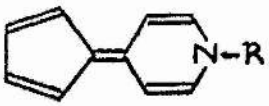
XVII b



XVIII



XIX



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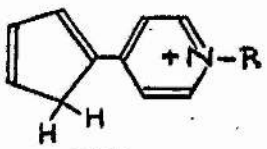

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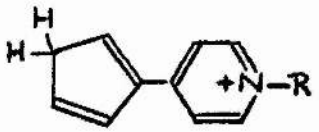

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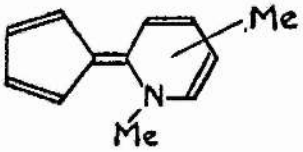

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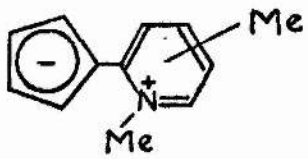

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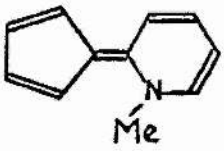

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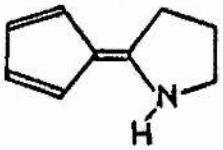
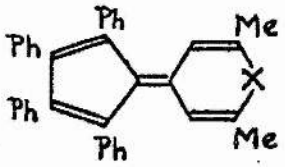
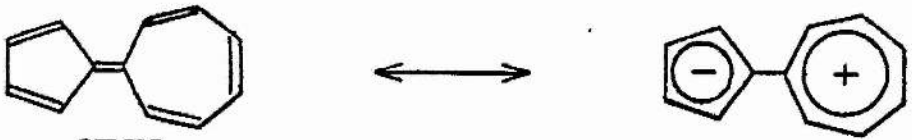


XXIII



XXIV



XXV a

XXV b

cyclopentadienones polymerise too rapidly to the corresponding dicyclopentadiene derivatives to be isolated at room temperature.

Related to the cyclopentadienylides are the cyclopentadienylidene derivatives in which the hetero-atom is separated from the five-membered ring by a conjugated chain of carbon atoms as in (XVIII, XIX; X = NR, O, S). Compounds of this type have only been prepared and studied comparatively recently. Thus in 1956 Krohnke[37] prepared the 4-cyclopentadienylidenedihydropyridine (XVIII; X= N(o,o'-dichlorobenzyl)). It has since been suggested[38] that the reported compound might in fact be a mixture of isomers corresponding to (XVIII) and (XIX). A year later Kursanov[39] was able to prepare unambiguously N-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (XIX, X = NCH_2Ph) by the reaction between N-benzylpyridinium chloride and lithium cyclopentadienide. Any ambiguity of its structure was eliminated by an alternative synthesis from 1-benzyl-4-bromopyridinium bromide[40,41] and its degradation to isonicotinic acid. Boyd[42,43] has developed a fairly general method for the preparation of 4-cyclopentadienylidene-dihydropyridines and their corresponding indenylidene[43] and fluorenylidene[43] analogues. Protonation of the coloured compounds (XX) led to colourless solutions which were shown

by N.M.R. to contain the isomers (XXa) and (XXb). Recently Boyd has prepared a series of 2-cyclopentadienylidene - N - methyl - 1,2 - dihydropyridines (XXI) with methyl groups in various positions of the pyridine ring[44]. N.M.R. studies showed that the protons of the 3-methyl group in (XXI, 3-Me) are abnormally deshielded and he has attributed this to the steric hindrance to coplanarity, suggesting that the molecule receives increased contribution from the dipolar pyridinium form (XXIb, 3-Me). The analysis of the N.M.R. spectra of 2-cyclopentadienylidene-N-methyl-1,2-dihydropyridine (XXII) and 2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (XXIII) has been described[45], and the barriers to rotation about the exocyclic double bonds in these compounds have been reported as 11.4 K.cal. and 19.6 K.cal. respectively, indicating a greater contribution from the dipolar form in (XXII).

In the oxygen series no compounds of type (XVIII ; X = O) have been reported. Of the compounds (XIX ; X = O) some benzo-analogues have been reported[43,46] while Lloyd and Wasson have prepared cyclopentadienylidenepyrans (XXIV) by the reaction of phenylated diazocyclopentadienes with 4-thiopyrones[47]. The same method was used to prepare cyclopentadienylidene thiopyrans (XIX ;X = S). Other substituted cyclopentadienylidenepyrans have recently been

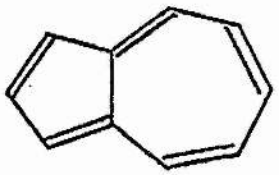
prepared[48].

The cyclopentadienylidene derivatives are iso-π-electronic with cyclopentadienylideneheptatriene (sesquifulvalene) (XXV) in which a five-membered ring is attached to a seven-membered ring. Theory predicts a large contribution from the dipolar form (XXVb) resulting in stabilisation, but as yet the parent compound has not been isolated although some substituted sesquifulvalenes have been prepared[49,50].

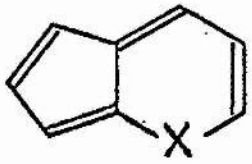
Cyclopentadiene condenses with aldehydes and ketones in the presence of a strong base to give a class of compounds known as fulvenes (XVII; X = CR_2). Most aspects of fulvene chemistry have been extensively reviewed including a very recent review by Bergmann[51]. The electron attracting tendency of the ring to acquire a stable sextet of π-electrons has been confirmed by dipole moment measurements. Thus the parent compound fulvene (XVII; X = CH_2), an unstable compound which readily polymerises, has a dipole moment of 1.1D[52], and dimethylfulvene (XVII, X = CMe_2) has a dipole moment of 1.48D[53]. These low dipole moments indicate a small contribution from the dipolar form. With substituents of electron donating character at the 6-position the contribution of the dipolar form becomes more significant[54,55]. Thus 6-dimethylaminofulvene (XXVI) has a dipole moment of

Plate 5

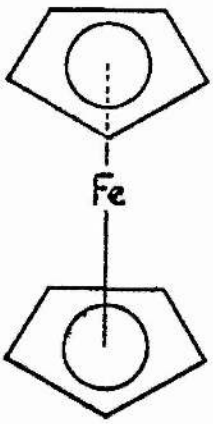
XXVI



XXVII a



XXVII b



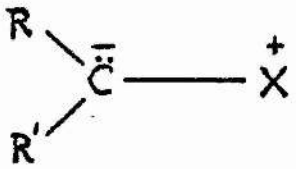
XXVIII

4.5D[56] and the polarity of the exocyclic double bond has been demonstrated by a number of workers who have studied its N.M.R. spectrum at various temperatures. Chemical evidence for the polarity of the exocyclic double bond in fulvenes is apparent from the ease with which they are reduced by lithium aluminium hydride[57], and the addition of organo-metallic compounds to yield substituted cyclopentadienes[58].

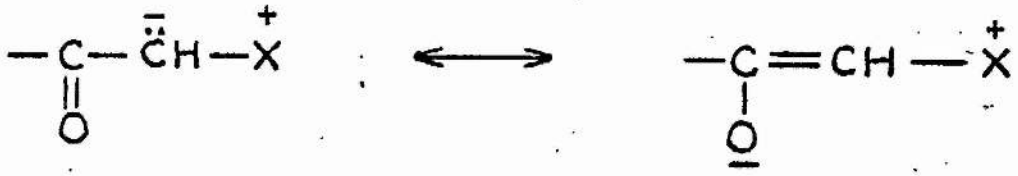
Other systems which involve the cyclopentadienide ring are the azulenes derived from the parent hydrocarbon bicyclo - [5,3,0] decapentaene or azulene (XXVIIa), and the pseudo azulenes e.g. (XXVIIb). Azulene chemistry has developed rapidly in the last twenty-five years and some extensive reviews have been published[59]. The cyclopentadienide character of the five-membered ring is shown by the readiness with which it undergoes electrophilic substitution.

In the case of ferrocene[60] (XXVIII) its properties suggest that the overall electron distribution in the molecule is such that the rings are nearly neutral[61]. Ferrocene and its derivatives cannot be considered purely as simple non-benzenoid aromatic compounds.

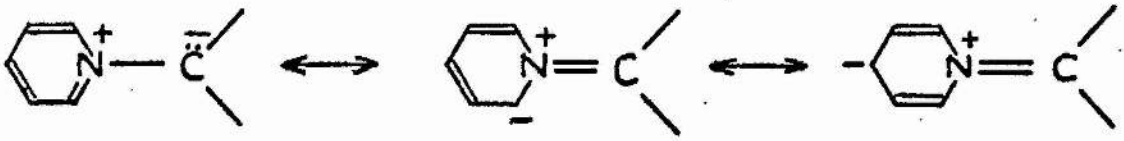
Plate 6



XXIX



XXX



XXXI

XXXII

2. CYCLOPENTADIENYLIDES (FLUORENYLIDES & INDENYLIDES).

An ylide can be defined as a substance containing a carbanion attached directly to a positively-charged hetero-atom, represented by the general formula (XXIX). Included in this definition are ylides which have an enolate structure (XXX) in which the carbonyl group can delocalise the negative charge of the carbanion, affording greater stability upon the ylide. Increased delocalization and hence increased stability is also achieved when the carbanion is part of the cyclopentadiene, fluorene or indene ring systems which have stable sextets of π-electrons.

The fact that some ylides are sufficiently stable to be isolated is a direct result of delocalisation of the non-bonded electrons of the carbanion. Stabilization of the carbanion can be afforded by the two carbanion substituents R (XXIX) as indicated, and also by the hetero-atom group X (XXIX). The hetero-atom itself can be nitrogen, phosphorus, arsenic, antimony, sulphur, and also as described in this thesis, bismuth and selenium. In the cases where X is an ammonium group it is generally assumed that stabilis-ation of the adjacent carbanion only occurs by electrostatic interaction between the opposite charges. Stability appears to be greater however when X is a pyridinium group. This

is probably due to stabilisation of the carbanion by resonance interaction with the pyridinium ring (XXXI) as well as by electrostatic interaction. The chemistry of diazo compounds, best represented by (XXXII), is such that they can be considered as special examples of nitrogen ylides. They display the nucleophilicity and thermal instability associated with nitrogen ylides and in analogous reactions afford similar if not identical products. Generally diazo compounds are more stable than the corresponding ammonium and pyridinium ylides.

Nitrogen, a first row element with filled 2s- and 3p- orbitals, has as its next available empty orbital the 3s- orbital. The energy of this orbital is too high for effective overlap with the non-bonded electrons of the carbanion and valence shell expansion of the nitrogen atom cannot occur. In contrast, the second row elements, phosphorus and sulphur, with filled 3s- and 3p- orbitals, have the 3d- orbitals as their next available empty orbitals. These orbitals are at an only slightly higher energy level and are consequently more available for overlap with the carbanion non-bonded electrons resulting in considerable stabilisation. The carbanion can take advantage of the ability of the phosphorus atom to expand its outer shell to accommodate ten electrons; the stabilisation afforded by a

sulphonium group is similarly attributed to overlap of the carbanion with the vacant, low energy d-orbital. There is considerable experimental evidence indicating that phosphorus can use its 3d-orbitals in σ-bonding and the pentacovalent phosphorus atom is well known. Although the involvement of d-orbitals of phosphorus in π-bonding has not been proved the $p\pi$-$d\pi$ bonding proposal accounts for much experimental data and is certainly justified until proved inadequate. Experimental evidence for d-orbital overlap in sulphonium ylides has been accumulated by estimating the degree to which stabilisation of an adjacent carbanion is due to conjugative interactions. These estimates have been made available by comparing the physical and chemical properties of ternary sulphonium salts with those of quaternary ammonium salts, and involve the reasonable assumption that the coulombic effects of the two groups are similar. Craig et al.[62-64] have predicted theoretically that a sulphonium group should provide effective stabilisation for an adjacent carbanion by an electron-accepting conjugative mechanism.

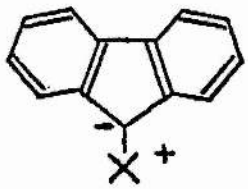
The properties of arsenic and antimony are similar to those of phosphorus and similar stabilisation of an adjacent carbanion by overlap of the d-orbitals can be expected. Whether overlap of the 4d- and 5d-orbitals of neutral

arsenic and antimony respectively can provide effective stabilisation is uncertain. However conversion of the arsine or stibine into a quaternary salt will force the central atom to carry a high degree of positive charge and thereby contract the normally diffuse d-orbitals such that effective overlap with the 2p-orbital of carbon should occur.

Although cyclopentadienylides (XXXIII) have only been described during the last fifteen years the analogous fluorenylides (XXXIV) have been known since 1911 when Staudinger prepared 9-diazofluorene[65] (XXXV). This is a red solid which melts without decomposition at 95° . It undergoes many reactions typical of a nitrogen ylide such as rapid reaction with nitrosobenzene[66,67] at room temperature to afford a nitrone, and reaction with carbenes[68] to yield the corresponding methylene fluorenes. Thus the diazo compound must be acting as a nucleophile and therefore, essentially, as an ylide. Staudinger also found that diazofluorene reacts additively with triphenylphosphine[69] to form a phosphazine (XXXVI), a reaction of stabilised diazo compounds which has become well known since this report. 9-Diazofluorene also undergoes numerous reactions in which the loss of nitrogen is involved and some of these reactions will be discussed in Section 3, Part I.

Plate 7

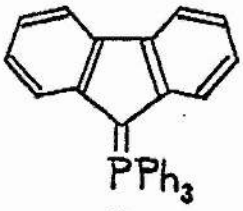
XXXIII



XXXIV

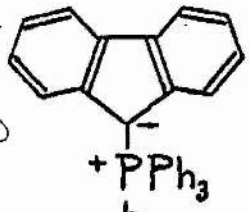
XXXV

XXXVI

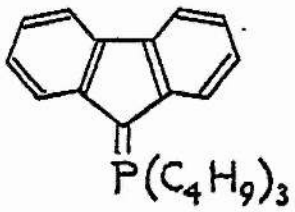


a.

XXXVII

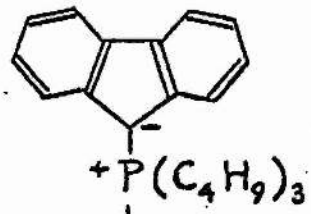


b.



a.

XXXVIII



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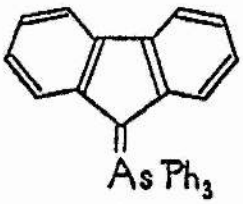
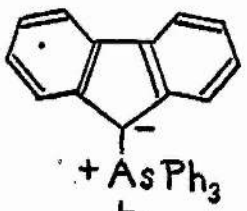


a.

XXXIX



b.

Ingold and Jessop prepared 9-dimethylsulphonium (XXXIV; X = SMe_2) fluorenylide[70], a compound which has since been studied by Johnson and LaCount[71], by the action of aqueous sodium hydroxide on fluorenyldimethylsulphonium bromide. This preparation, treatment of an 'onium salt with a suitable base, is an example of the most general method for the preparation of ylides and has been called the 'salt method'. The same workers were unable to isolate trimethylammoniumfluorenylide[72](XXXIV; X = NMe_3); in accord with earlier discussion it was much less stable than the corresponding sulphonium ylide. In fact it could only be prepared under nitrogen[73,74]. Similar instability was found for 9-pyridinium fluorenylide[75] (XXXIV; X = C_5H_5N) although some of its reactions have been studied[76,77] and the dipole moment of the crude ylide has been reported as 4.13 D[78], a value which seems too low compared with other fluorenylides. Introduction of an electron-withdrawing group into the fluorene portion of the molecule will stabilise the resulting ylide and pyridinium 2-nitro-fluorenylide has been isolated as a blue-green solid[79] stable in the absence of air and light.

A number of phosphonium fluorenylides have been prepared by the standard salt method and their chemical and physical properties studied. Triphenylphosphonium fluorenylide[80] (XXXVII), a stable high melting solid, has a dipole moment

of 7.09 D suggesting that there are nearly equal contributions from the dipolar and covalent forms. Johnson and LaCount have made an interesting comparative study[81] of the triphenyl- and tri-n-butylphosphonium fluorenylides. Whereas the triphenyl ylide was stable and melted at 259° the tributyl ylide (XXXVIII) melted at 124° and was slowly decolourised on exposure to the atmosphere. The pK_a's of the two ylides determined spectroscopically in 31% water/dioxan indicated that the triphenyl ylide (pK_a = 7.5) was less basic and thus less nucleophilic than the tributyl ylide (pK_a = 8.0). The greater nucleophilicity of the tributyl ylide was confirmed by comparing the reactivity of the two ylides with carbonyl compounds. The tributyl ylide reacted faster with aromatic aldehydes and also reacted with activated aromatic ketones with which the triphenyl ylide did not react. The conclusion drawn from these results was that the triphenylphosphonium group is better able to delocalise the negative charge of the carbanion than is the tributylphosphonium group. In other words, the 3d-orbitals of the triphenylphosphonium group must provide better overlap with the filled 2p-orbital of the carbanion than the 3d-orbitals of the tributyl- phosphonium group. The dipole moments μ = 7.09 D (triphenyl ylide) and μ = 7.39 D (tributyl ylide) suggest that there is more double bond character in the carbon-phosphorus bond

of the triphenyl ylide than in that of the tributyl ylide which is consistent with this conclusion[82].

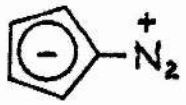
Johnson has also made a detailed examination of the chemical and physical properties of triphenylarsonium fluorenylide[83] (XXXIX) and he has compared these with the properties of (XXXVII). The arsonium ylide was a pale yellow crystalline compound, melting point 190°, which was slowly hydrolysed after standing exposed to the atmosphere for about one month. Its pK_a determined spectroscopically was 7.8 compared with 7.5 for the analogous phosphonium ylide. A comparative study of the reactivity of (XXXIX) and (XXXVII) with carbonyl compounds was carried out and it was found that the arsonium ylide was more reactive than the phosphonium ylide. The conclusion reached from these and other physical and chemical properties is that triphenylarsonium fluorenylide is more basic than the phosphonium analogue and that (XXXIXb) contributes more to the actual structure of the arsonium ylide than does (XXXVIIb) to the actual structure of the phosphonium ylide.

Wittig and Laib have prepared trimethylarsonium fluorenylide[84] but it was handled entirely in solution and was not isolated. The same workers attempted to prepare the stibonium analogue but could only isolate bifluorenyl from the reaction mixture.

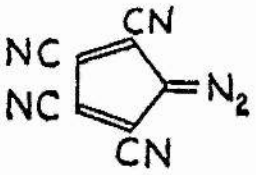
The first such cyclopentadiene derivative to be reported was the remarkably stable diazocyclopentadiene (XL) prepared by treating cyclopentadienyl lithium with p-toluenesulphonazide[85]. A recent modification of this method[86] involves the treatment of cyclopentadiene and p-toluene-sulphonazide with a suitable base such as diethylamine. Phenylated diazocyclopentadienes have been similarly prepared,[87] but a superior method has been reported by Regitz and Liedhegener in which a suspension of the diene in acetonitrile is treated with p-toluenesulphonazide in the presence of piperidine[88]. This method gives almost quantitative yields of the required phenylated diazocyclopentadiene. Tetrachloro-[89] and tetracyanodiazocyclopentadienes[23] (XLI) have also been prepared. In the latter compound the stabilising power of the cyano groups coupled with that of the 6 π-electron cyclopentadienide system are the major factors in determining which resonance form, (XLIa) or (XLIb), will contribute most to the structure. Webster suggests that, with the high dipole moment (11.44 D) and its stability to acid conditions (it can be recovered from concentrated sulphuric acid solutions), tetracyanodiazocyclopentadiene behaves as a diazonium compound rather than a diazo compound[23].

The aromatic character of diazocyclopentadiene has been confirmed both by its physical and its chemical properties.

Plate 8

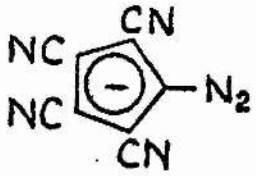


XL



a.

XLI



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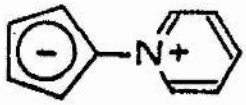
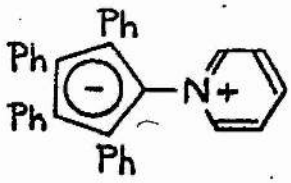
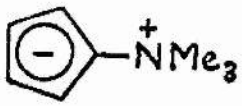


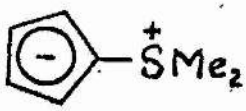
XLII



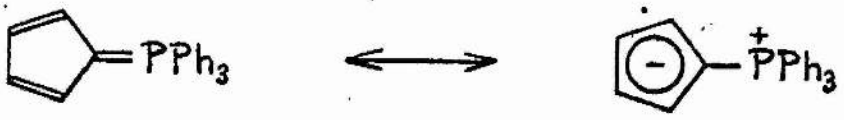
XLIII



XLIV



XLVI



XLV

The N.M.R. spectrum consists of two equivalent unsymmetrical quartets corresponding to an A_2X_2 system, with chemical shifts of 3.3τ and 4.2τ[90] or 3.38τ and 4.14τ[91]. The absorption at 3.3τ has been assigned to the protons at the 2,5-positions since the electron-withdrawing diazo group exerts a stronger deshielding influence on these positions. Diazocyclopentadiene readily undergoes electrophilic substitution reactions with attack occuring preferentially at the 2,5-positions presumably because a more stable transition state is involved at these positions[90]. 2,3,4-Triphenyldiazocyclopentadiene also undergoes a number of electrophilic substitution reactions; protonation in strong acid has been shown from the N.M.R. spectrum to take place at the 5-position[87].

Diazocyclopentadienes, with the exception of 2,5-diphenyldiazocyclopentadienes[92], react additively with triphenylphosphine, to form the corresponding phosphazines. The thermal or light induced decomposition of diazocyclopentadienes to form carbenes as intermediates is well known and some of these reactions are mentioned in the next section.

In 1955 Lloyd and Sneezum prepared pyridinium cyclopentadienylide[93] (XLII) by the action of pyridine on dibromocyclopentene and treatment of the resulting salt with alkali. It is a crystalline solid which appears to be stable

indefinitely if kept under nitrogen. The same workers[94] prepared the tetraphenyl analogue (XLII) by reaction of pyridine with 5-bromo-1,2,3,4-tetraphenylcyclopentadiene and subsequent treatment with alkali. No ylide could be isolated when 2-methyl- or 2,6-dimethylpyridines were used, presumably owing to steric hindrance between the α-methyl and phenyl groups. When 1-bromoindene was treated in the same manner a material which gave only a transient blue colour in chloroform was obtained[94]. Thus, like the corresponding fluorenylide, pyridinium indenylide appears to be unstable. The pyridinium cyclopentadienylides are intensely coloured and the colours of their solutions in various solvents depend on the polarity of the solvents. Kosower and Ramsey[95] studied the ultra-violet and visible spectrum of (XLII) in a variety of solvents and ascribed a band at 5000 Å to intra-molecular charge transfer. The pK_a of the ylide conjugate acid was found to be 10.0 and its dipole moment has been reported as 13.5 D[96].

Shortly after Lloyd and Sneezum's description of (XLII) the corresponding trimethylammonium- (XLIV)[97] and triphenylphosphonium cyclopentadienylides (XLV)[98] were reported. The trimethylammonium ylide decomposes on prolonged contact with air whereas the phosphonium ylide appears to be stable indefinitely. The latter compound is remarkably unreactive

being unaffected by boiling alcoholic potassium hydroxide and inert to carbonyl compounds in the Wittig reaction[99]. Oda et. al.[100] have prepared triphenylphosphoniumindenylide and compared its reactivity with the analogous fluorenylide and cyclopentadienylide towards dichlorocarbene. The fluorenylide gave a 44% yield of olefin, the indenylide 8%, and the cyclopentadienylide did not react. They suggested that this is due to the relative difficulty in the localisation of one electron pair on the ∝-carbon atom and that this explains the inertness of (XLV) in the Wittig reaction.

Dimethylsulphoniumcyclopentadienylide (XLVI) has been reported recently[101] and has a dipole moment of 5.7 D compared with 6.99 D for the corresponding phosphonium ylide. This indicates a larger contribution from the covalent form in (XLVI).

Many electrophilic substitution reactions have been carried out on the cyclopentadienylides. The pyridinium, trimethylammonium, and triphenylphosphonium ylides can be brominated [85,97,102], they couple with diazonium salts[94,97,99], and the triphenylphosphonium ylide has been formylated and acetylated[103].

3. CARBENES.

Several review articles[104-109] and monographs[110,111] have been published concerning most aspects of carbene chemistry. This section gives a brief introduction to the electronic structure and formation of carbenes, and especially the reactions of carbenacyclopentadienes and 9-carbenafluorene, and finally the formation of ylide intermediates in carbene reactions.

(i) Electronic Structure of Carbenes.

The structural problems of carbenes are increased by the fact that there are two relatively low-lying electronic states. Considering carbene (CH_2) as the simplest member of the series, it is obviously electron-deficient since carbon atoms have four low-energy bonding orbitals. Two of these orbitals are used by the four C-H bonding electrons leaving two more for occupation by the two non-bonding electrons. If the remaining two orbitals are equivalent, the electrons, according to Hund's rules, should be assigned to different orbitals with parallel spins. Alternatively, if the two available orbitals are not degenerate the electrons would be expected to occupy the orbital of lower energy with spin-pairing. The species with unpaired spins would have a net electronic spin angular momentum of unity and would therefore be a triplet state. The species with spin-paired non-bonding

Non-Bonding Orbitals

Bonding Orbitals

Singlet State CH_2:

Triplet State CH_2:

Fig 3.1 Electronic states for the low-energy orbitals in carbene

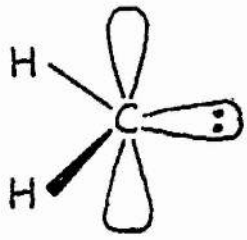


Fig 3.3

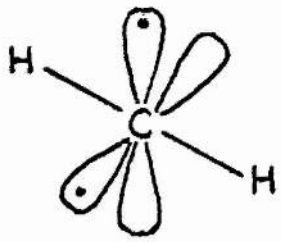


Fig 3.2

Fig 3.4

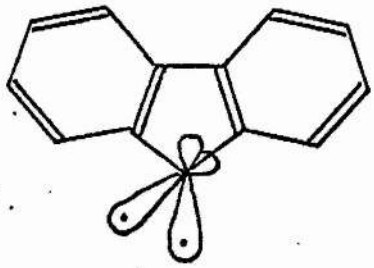


Fig 3.5

electrons would be a singlet state. The relationships are shown in Fig. 3.1. Triplet carbene would contain linear sp-hybridised carbon-hydrogen bonds with the unpaired electrons in two orthogonal p-orbitals (Fig. 3.2). Singlet carbene is most likely to have a configuration involving sp^2-hybridisation of the carbon atom[112] with the paired non-bonding electrons occupying one of the sp^2 hybrid orbitals and leaving the carbon atom with a vacant p-orbital (Fig. 3.3).

The problem which arises from the possibility of two low-lying electronic states for carbenes is to decide the nature of the ground state.

Recently electron spin resonance measurements have been used to characterise the ground states of aryl carbenes. This technique has indicated that carbenacyclopentadiene[113] (Fig. 3.4) and 9-carbenafluorene[114] (Fig. 3.5) have triplet ground states. In these two carbenes, which are structurally similar, steric strain of the carbene carbon atom will prohibit a linear sp-hybrid structure, and most likely a sp^3-hybridised structure will be adopted.

(ii) Formation of Carbenes.

Two common types of carbene-forming reaction are the thermal or photolytic decomposition of diazoalkanes and ketones, and base-catalysed α-elimination reactions. An example of this latter method is the formation of dichlorocarbene from

chloroform and base (usually potassium tert.-butoxide).

The method used to decompose a particular diazo compound will generally depend on its stability. Thus simple diazoalkanes such as diazomethane and diazopropane are best decomposed photolytically owing to their explosive nature. However for the more stable diazo compounds such as diphenyldiazomethane, 9-diazofluorene and the phenylated diazocyclopentadienes, thermal decomposition is often the preferred route to the corresponding carbene. Temperatures in the range 60-180° are usually required for decomposition depending on the particular diazo compound.

(iii) Carbenacyclopentadienes and 9-carbenafluorene.

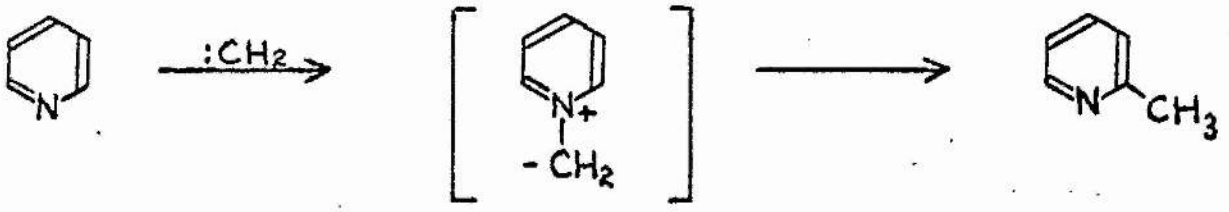
The reactions of carbenes fall into two main categories, namely, insertion and addition reactions. Insertion reactions of carbenes occur at a saturated C-H or C-Cl bond, while addition reactions occur mainly with carbon-carbon double bonds leading to the formation of cyclopropane derivatives. The addition of electrophilic carbenes to hetero-atoms with a lone pair of electrons to form ylide intermediates is discussed later. For both addition and insertion reactions the electronic nature of the carbene determines the rate and stereochemistry[115] and this aspect of some reactions of carbenacyclopentadienes and 9-carbenafluorene has been studied.

The photolysis of diazocyclopentadiene in cyclohexane[116] to give insertion products was the initial evidence of the

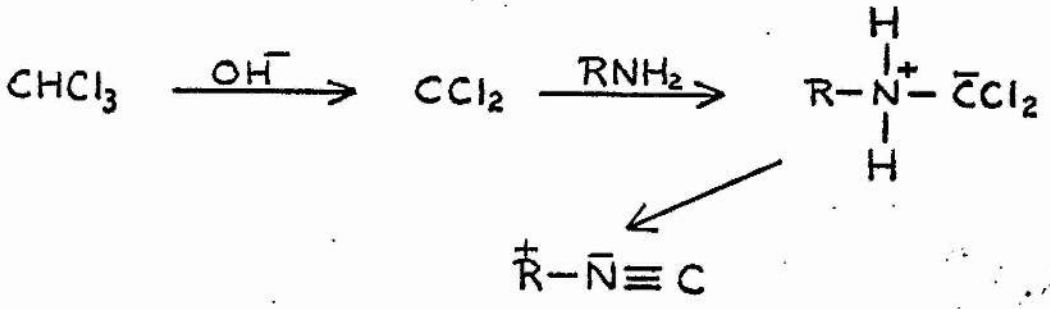
formation of carbenacyclopentadiene as an intermediate. Subsequently the diazo compound was photolysed in various matrices[117] at low temperatures but except for evidence of the formation of fulvalene the electronic spectra were ambiguous. Low temperature photolysis coupled with E.S.R. observation however demonstrated that the carbene is a triplet in its ground state[113]. Unfortunately these elegant experiments allow no conclusions as to the identity, chemical properties or spin multiplicity of the initial intermediate derived from the photo-excitation of diazocyclopentadiene.

Moss has done experiments[118] in which he decomposed diazocyclopentadiene photolytically in various saturated and unsaturated hydrocarbons. The products and mode of their formation suggested that carbenacyclopentadiene was reacting in the singlet state. In similar reactions with tetrachloro-diazocyclopentadiene McBee[119] has said that the intermediate carbene shows triplet character owing to the non-stereospecific addition to olefins. He agreed with Skell's postulate[112] that stereospecific addition indicates a singlet state but considered that the corollary, that non-stereospecific addition indicates a triplet state, is not justified. Dürr and Scheppers[121] have found that stereospecific addition does occur for carbenatetraphenylcyclopentadiene and that this indicates singlet character. This carbene was also found to

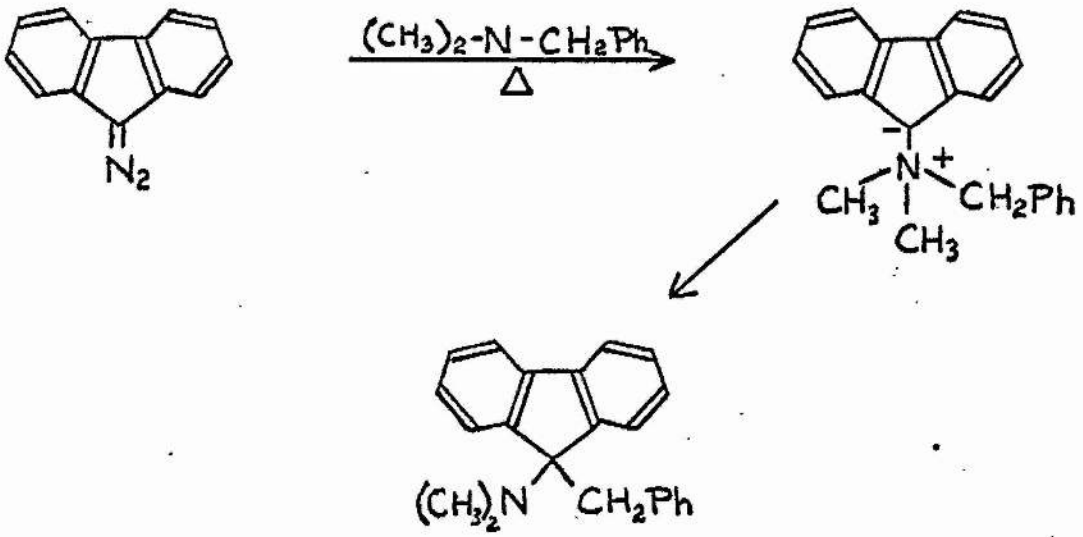
Plate 10



(3·6)



(3.7)



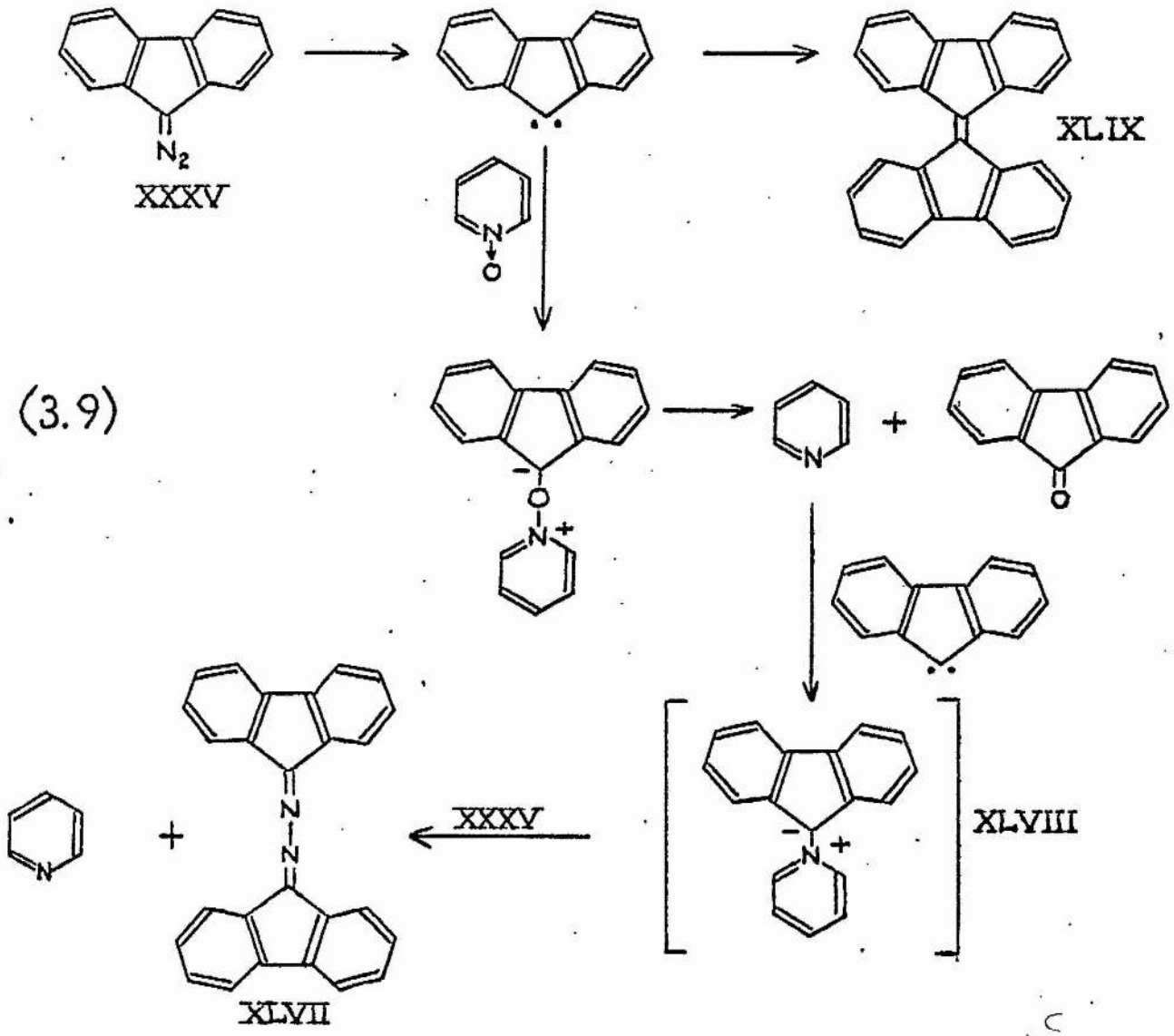
(3.8)

insert in mesitylene.[122] 9-Carbenafluorene has a triplet ground state as shown by E.S.R. measurements[114]. Its reactions with olefins also indicate that the reacting species is in a triplet state. Moritani et. al.[123] have shown that the carbene adds non-stereospecifically to diethyl malęate (cis-olefin) and diethyl fumalate (trans-olefin). Although light-induced stereoisomerisation was reported to occur when cis- and trans-butenes were used as olefins[124], this complication was not found in the above case[125].

In conclusion it is obvious that much additional study is required before comprehensive generalisations concerning the characteristic reactivity of singlets and triplets can be warranted.

(iv) Ylide Intermediates in Carbene Reactions.

It seemed likely that the electrophilic carbenes would attack a hetero-atom with an available lone pair of electrons to form an ylide. There is strong evidence for insertion reactions proceeding via ylide intermediates for some carbene-amine reactions. Carbene reacts with N-methylpyrrolidine in a non-specific manner[126] to give a number of products whereas with pyridine it gives an 83% yield of ∝-picoline (3.6)[127]. The well known 'carbylamine reaction' which involves treating a primary amine with chloroform and strong base proceeds via an ylide intermediate (3.7). One of the earliest known



(3.10) $CHCl_3 \xrightarrow{KOBu^t} [:Cl_2] \xrightarrow{PPh_3} Ph_3P{=}CCl_2$ L

$\downarrow (C_6H_5)_2CO$

$(C_6H_5)_2C{=}CCl_2 + Ph_3PO$

(3.11) $(CH_3)_3\overset{+}{N}-\bar{C}H_2 \longrightarrow [:CH_2] \xrightarrow{PPh_3} Ph_3P{=}CH_2$ LI

$\downarrow (C_6H_5)_2CO$

$(C_6H_5)_2C{=}CH_2 + Ph_3PO$

reactions of 9-carbenafluorene involved the formation of an ylide intermediate by attack on benzyldimethylamine which then underwent a Stevens rearrangement (3.9).[128] Schweizer has studied the deoxygenation of some pyridine N-oxides using diazofluorene in benzene[129]. Amongst his products he isolated a high yield of the ketazine (XLVII) which he concluded was formed from reaction of the ylide intermediate (XLVIII) with more of the original diazofluorene. Schweizer suggested that (XLVIII) is formed from 9-carbenafluorene and pyridine and this is supported by the fact that when 2,6-dimethylpyridine N-oxide is used there is an increased yield of bifluorene (XLIX) and a decreased yield of ketazine. In other words the reaction of 2,6-dimethylpyridine with 9-carbenafluorene is retarded due to the steric hindrance of the methyl groups. His suggested reaction path (3.9)[129] is shown schematically on Plate 11.

The first deliberate attempt to prepare an ylide from a carbene was carried out in 1960 when Speziale[130] trapped dichlorocarbene with triphenylphosphine to afford a yellow suspension of the ylide (L). He confirmed the presence of (L) by adding benzophenone to the solution and isolating 1,1-dichloro-2,2-diphenylethylene(3.10). Shortly after this report analogous reactions were carried out by Seyferth et.al.[131] and Wittig and Schlosser[132]. Franzen and Wittig[133]

have found that trimethylammoniummethylide dissociates to trimethylamine and carbene since the latter could be trapped with cyclohexene to afford norcarane. They also found that addition of triphenylphosphine and benzophenone in place of cyclohexene afforded diphenylethylene (3.11) presumably via the intermediate formation of the ylide (LI).

In all examples cited the intermediate ylides have not been capable of isolation owing to their high reactivity. Most of Part II and Part III of this thesis concerns the preparation and isolation of a number of new cyclopentadienylides by the thermal decomposition of diazotetraphenylcyclopentadiene in the presence of suitable nucleophilic reagents, together with an investigation of their properties.

PART II

DISCUSSION

1. TETRAPHENYLCYCLOPENTADIENYLIDES

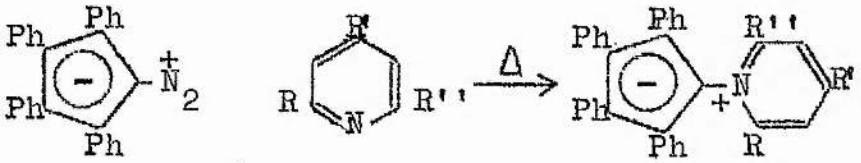
(i) Thermal decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene

Some preliminary work by Band, Lloyd, and Wasson[138] had shown that 2,3,4,5-tetraphenyldiazocyclopentadiene, when heated to reflux in pyridine, gave a blue solution which appeared to contain pyridinium 2,3,4,5-tetraphenylcyclopentadienylide (1). The body of this thesis is concerned with the investigation of the reaction of 2,3,4,5-tetraphenyldiazocyclopentadiene with compounds containing a hetero-atom with a lone pair of electrons to give ylides, and the study of the properties and reactions of these ylides.

The preparation of 2,3,4,5-tetraphenyl- and 2,3,4-triphenyldiazocyclopentadienes has been described in the literature but during the course of this work a superior method was reported by Regitz and Liedhegener[88]. The method involves treatment of a suspension of the corresponding cyclopentadiene in acetonitrile with p-toluenesulphonylhydrazine and piperidine. Mild conditions are used and after three hours a high yield of the diazo compound is obtained. Experimental details with minor modifications are given in Part III.

Pyridines.- A solution of 2,3,4,5-tetraphenyldiazo-

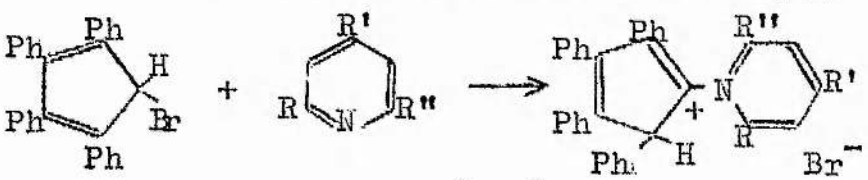
cyclopentadiene in pyridine was heated to reflux under an atmosphere of nitrogen. Nitrogen was evolved from the reaction and the red solution gradually became darker until it was blue-purple. The course of the reaction could be followed by periodically examining the infra-red spectrum of a sample removed from the reaction mixture. 2,3,4,5-Tetraphenyldiazocyclopentadiene has a characteristic strong absorption at 2100 cm^{-1} due to the diazo group and after the mixture had been refluxed for fifteen minutes the infra-red spectrum showed the absence of this peak which indicated complete decomposition of the diazo compound[139]. Owing to the ready



(1) R=R'=R''=H
(2) R=R''=H;R'=Me
(3) R=R'=H;R''=Me
(4) R'=H;R=R''=Me

(2.1)

decomposition of pyridinium 2,3,4,5-tetraphenylcyclopentadienylide (1) in solution it was quickly isolated by adding water, in which it is insoluble, to the reaction mixture and washing well with water to remove any pyridine. By this method a yield of over 90% of the crude blue ylide was obtained. Lloyd and Sneezum[93,94] had previously prepared (1) by the action of alkali on the bromide (5), thus.-



(5) R=R'=R''=H
(6) R=R''=H;R'=Me
(7) R=R'=H;R''=Me
(8) R'=H;R=R''=Me

(2.2)

They also obtained (6) in 80% yield but only isolated 6% of (7) and were unable to detect any of (8). This was presumably due to the steric over-crowding which would occur in the five-membered transition state leading to salt formation. However, decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in γ-picoline, α-picoline, and 2,6-dimethylpyridine resulted in yields of over 90% of (2), (3), and (4) respectively, indicating no such inhibition of attack.

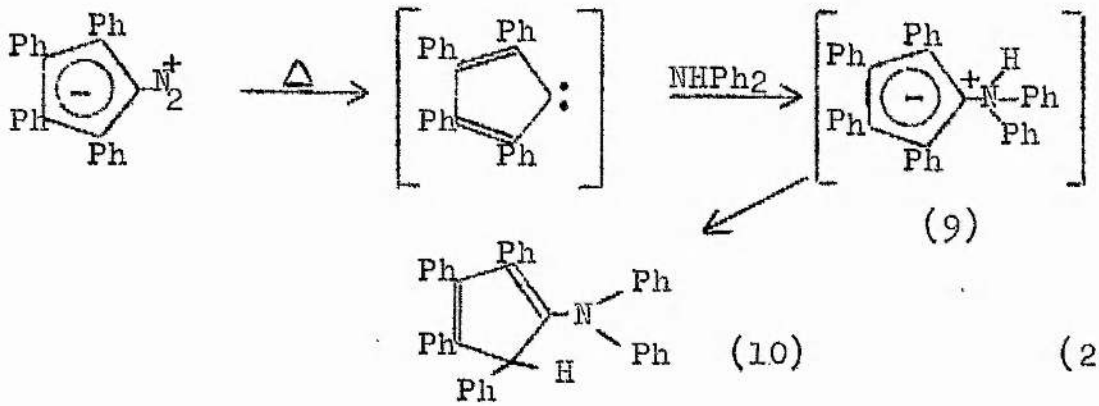
No suitable solvent could be found from which to recrystallise these ylides but they were soluble in 60% perchloric acid and gave stable yellow crystalline perchlorates which were readily characterised. The ylides all showed a bathochromic shift in the ultra-violet and visible spectrum of about 60-70 mμ from methanol to benzene.

2,3,4,5-Tetraphenyldiazocyclopentadiene melts with decomposition at a temperature $\geq 140^{\circ}$ presumably with the initial loss of nitrogen to give a carbene. The decomposition temperature might be expected to be lower when the diazo compound is heated in a melt or a concentrated solution and it seems most likely that the mechanism by which the pyridinium ylides were formed proceeded via a carbene intermediate with attack on the lone pair of electrons on the pyridine. Ylide intermediates have been postulated for many reactions between carbenes and amines but have not before been isolated.

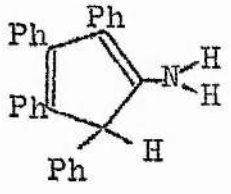
An example of such a reaction is the formation of α-picoline from pyridine and carbene[127]. (see Part I; Plate 10).

Diphenylamine. The reaction of N,N-dimethylbenzylamine[128] with diazofluorene carried out by Bamford and Stevens resulted in the isolation of 9-benzyl-9-dimethylaminofluorene, (see Part I; Plate 10). The product was explained by proposing that the diazo compound decomposed to fluorenylidene which was attacked by the amine to afford a new nitrogen ylide as an intermediate. This ylide would be expected to undergo a Stevens' rearrangement to the observed product.

A similar mechanism is suggested for the decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in diphenylamine, a low melting solid. The reactants were heated under nitrogen at 140° and a deep green melt was obtained, but after about fifteen minutes this had rapidly changed to brown. Chromatography of the reaction mixture gave a yellow amorphous solid in 50% yield which, from its physical properties, spectra, and analysis, and from its mode of preparation, was assigned the structure (10). This can be explained by the decomposition



of the diazo compound to 2,3,4,5-tetraphenylcyclopentadienylidene and subsequent attack by diphenylamine to give the nitrogen ylide (9), which could account for the deep green colour. This will then undergo a Stevens' rearrangement as above (2.3) to give 1-(N,N'-diphenylamino)-2,3,4,5-tetraphenylcyclopentadiene (10). The N.M.R. spectrum of the yellow solid showed a complex peak centred at 2.96τ arising from thirty phenyl protons and one sharp peak at 4.80τ due to one proton, corresponding to the position for the signal from a proton in an environment such as in (10)[140]. Its U.V. spectrum in cyclohexane had a maximum at 245mμ which could be assigned to the absorption of the cyclopentadienyl portion of the molecule and another maximum at 282mμ which could be assigned to the diphenylamino- absorption. The compound (10) was a yellow amorphous solid of low melting point (80°) which could not be satisfactorily recrystallised due to its high solubility in all common organic solvents. An analytical sample was prepared from a cooled solution of (10) in light petroleum. It is interesting to note that compound (10) has very similar physical properties to a compound prepared by Lloyd and Wasson which they considered to be 1-amino-2,3,4,5-tetraphenylcyclopentadiene (11)[141].



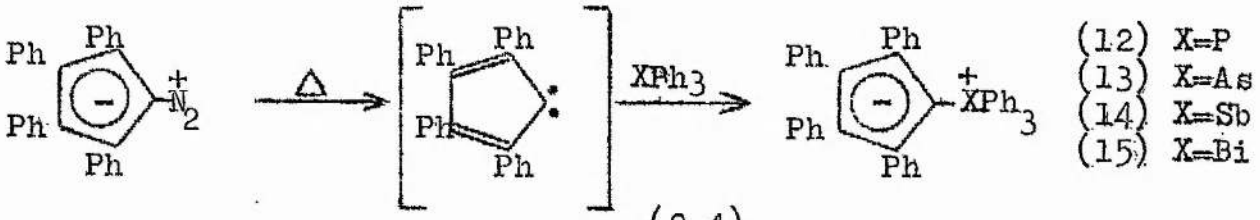
(11)

Triphenylamine.- No ylide or any other rearrangement products could be isolated from the reaction in which 2,3,4,5-tetraphenyldiazocyclopentadiene was heated to above 140° with triphenylamine. Probably in this case it was not possible for the tetraphenylcarbenacyclopentadiene to approach without steric hindrance because of the small radius of the nitrogen atom which was surrounded by three phenyl groups. Triphenylamine is a weak nucleophile and has a low dipole moment (0.26D).

Triphenylphosphine.- The high polarity of triphenylphosphine (μ=1.45D) is in keeping with its strong nucleophilic character, and the larger radius of the phosphorus atom, in contrast to the nitrogen atom, makes it possible for a fourth ligand to approach without steric hindrance. As the existence of (1-naphthyl)-triphenylphosphonium salts shows, very bulky ligands can be accommodated[142].

An earlier attempt had been made to isolate a product from the decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in the presence of triphenylphosphine but the reaction was done in a high-boiling solvent and no recognisable product was obtained[141]. Triphenylphosphine melts at 80° and it has been found that by heating a mixture of 2,3,4,5-tetraphenyldiazocyclopentadiene and triphenylphosphine at 140° there is a smooth loss of nitrogen with the formation of a high yield

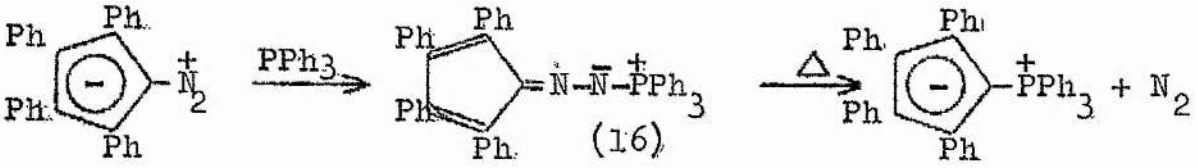
of triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide (12)[92]. The reaction is again considered to proceed



(12) X=P
(13) X=As
(14) X=Sb
(15) X=Bi

(2.4)

via a carbene intermediate (2.4). An alternative mechanism involves the initial formation of the phosphazine (16) which could then lose nitrogen to give the observed product.



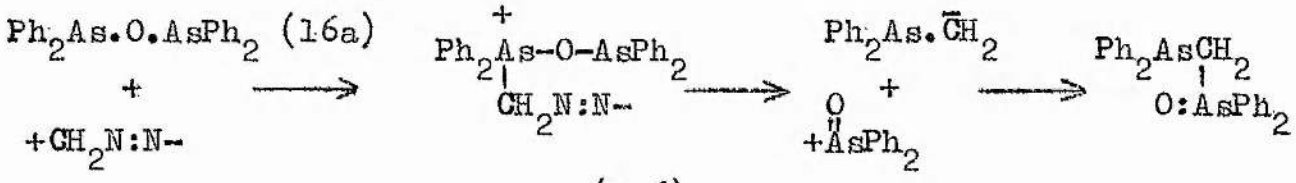
(16)

(2.5)

Reactions of this type are known and the earliest example was reported by Staudinger in 1919[69]. However this alternative has been discarded as a possibility as there was no evidence for the formation of (16) and later discussion (Part II,2,ii) indicates that the thermal decomposition of cyclopentadienylidenetriphenylphosphazines does not give the corresponding ylide. In particular Ramirez and Levy[143] were unable to isolate triphenylphosphonium cyclopentadienylide from the decomposition products of cyclopentadienylidenetriphenylphosphazine.

Triphenylarsine.- An analogous decomposition (2.4) was

carried out in triphenylarsine, a low-melting solid, and the corresponding ylide, triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (13) was obtained in good yield[144]. This reaction presumably again proceeded through the tetraphenylcyclopentadiene moiety, generated as a carbene, which then reacted with the lone pair of electrons on the arsenic atom. This represents a novel way of forming a carbon-arsenic bond and compound (13) is the first arsonium cyclopentadienylide to have been reported. The only related reaction in the literature is the mechanism postulated for the reaction between diazomethane and phenyldichloroarsine[145]. It was suggested that the phenyldichloroarsine was hydrolysed into diphenylarsine oxide (16a) which then reacted with diazomethane.



(2.6)

This experiment was done in ethereal solution at 0° and thus it is unlikely that the reaction was initiated by the decomposition of diazomethane to carbene which then might have attacked the oxide (16a) to form an intermediate arsonium ylide.

Triphenylstibine.- When 2,3,4,5-tetraphenyldiazocyclopentadiene was decomposed in triphenylstibine at 140° a 55% yield of triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (14) was obtained[146]. This is the first stibonium

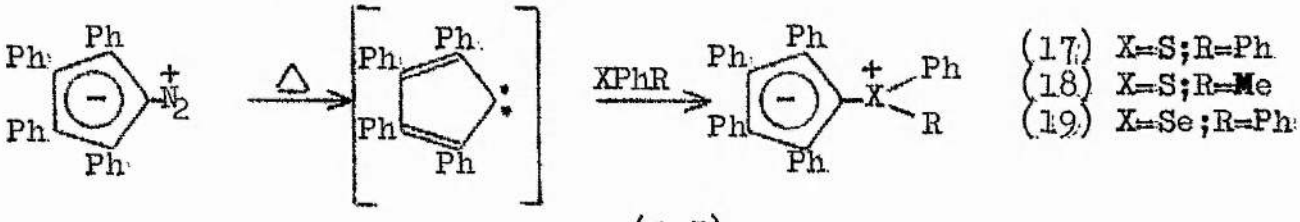
ylide to have been isolated although a few have been prepared in solution. Wittig and Laib[84] prepared dimethyldibenzylstibonium bromide which on treatment with an ethereal solution of phenyllithium afforded a yellow colouration which quickly faded. Wittig also prepared triphenylstibonium methylide in solution[147]. Although the ylide (14) is, at present, the only known stable stibonium ylide, pentacovalent derivatives of antimony have been known for some time.

Triphenylbismuth.- There are only three examples of pentacovalent bismuth compounds known, triphenylbismuth dichloride, pentafluorobismuth, and pentaphenylbismuth[148], and very few examples of quaternary bismuth salts have been reported. Wittig and Hellwinkel[148] claimed recently that triphenylbismuth reacted with chloramine-T to afford triphenylbismuthonium-N-tosylamine, $(C_6H_5)_3\overset{+}{B}i-\overset{-}{N}-SO_2-C_6H_4CH_{3(p)}$, but this substance was not isolated or characterised.

It seemed possible, in light of the previous reactions discussed, that decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in molten triphenylbismuth might give the bismuthonium ylide (15). The reaction mixture became deep blue and a crude blue solid was isolated. Thin layer chromatography indicated that apart from the blue compound the only other compound present was triphenylbismuth. Attempts to prepare an analytical sample of the substance by

chromatographic methods or by recrystallisation failed owing to its ready decomposition. However from its mode of preparation, its physical properties, and its spectra the blue solid was probably triphenylbismuthonium 2,3,4,5-tetraphenylcyclopentadienylide (15).

Diphenylsulphide and methylphenylsulphide.- The elements of the VIB subgroup, sulphur and selenium, are hetero-atoms which contain a lone pair of electrons in the divalent state and which should be liable to attack from a carbene to give ylides. Prior to the present work there were only two methods available for the synthesis of sulphonium ylides, the salt method (see Part I, Section 2) and the benzyne method[149]. It has been found that diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (17) and the methylphenylsulphonium analogue (18) can be successfully prepared in good yield by decomposing 2,3,4,5-tetraphenyldiazocyclopentadiene in diphenylsulphide[150] and methylphenylsulphide respectively.



(2.7)

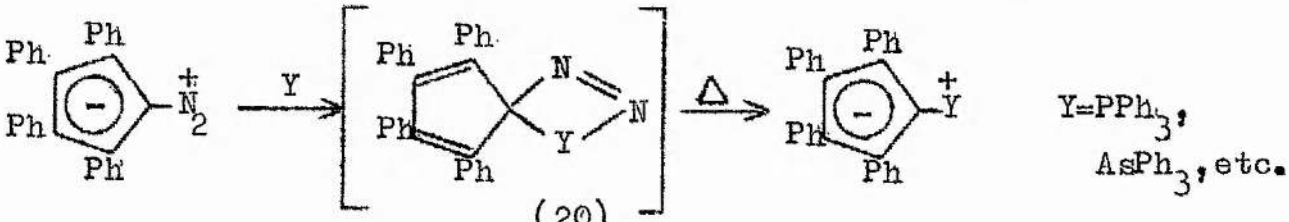
Diphenylselenide.- The only attempt to prepare a selenonium ylide was that reported in the literature by Hughes and Kuriyan[151]. They prepared fluorenyl-9-dimethylselenonium bromide and on treatment of this compound with alkali they

obtained a black precipitate, an unlikely colour for a selenonium ylide. The black substance was very unstable and decomposed rapidly at room temperature with the evolution of dimethylselenide.

Diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide (19) has now been prepared in 90% yield by the thermal decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in diphenylselenide, and is a stable crystalline solid.

(ii) Reaction Mechanism

The reactions discussed so far are considered to proceed via the intermediacy of 2,3,4,5-tetraphenylcarbenacyclopentadiene (23). However an alternative mechanism, although less likely, should be mentioned. This involves the initial formation of a cyclic intermediate (20) which might then rearrange with the loss of nitrogen to give the observed

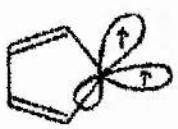


(20) (2.8)

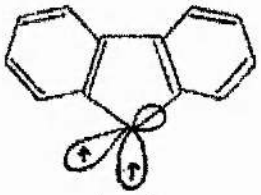
product. This mechanism seems unlikely for a number of reasons.- a) The formation of the cyclic intermediate (20) will be sterically unfavoured; b) the normal reaction of a phosphine with a diazo compound results in the formation of a phosphazine and there seems no reason why triphenylphosphine

should react in any other way with 2,3,4,5-tetraphenyldiazocyclopentadiene if it were to react at all before the loss of nitrogen; c) if this mechanism occurs then it would be expected that other diazocyclopentadienes might undergo similar reactions but this has been shown not to be the case (Part II,2).

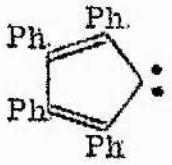
The thermal decomposition of diazo compounds with the initial formation of a carbene is well known and the reactions above are best explained on this basis. The ground states of carbenacyclopentadiene (21) and fluorenylidene (22) have been



(21)



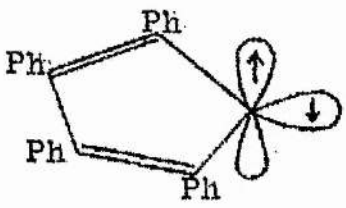
(22)



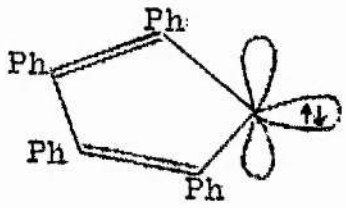
(23)

described as triplet on the basis of results obtained from their E.S.R. spectra[113,114]. Although the carbene (23) has not been similarly studied it may also have a triplet ground state. However the singlet state of (23) has been postulated for some of its reactions (Part I, Section 3) and the presently observed chemistry is most satisfactorily explained in terms of the singlet state. Moss[118] has discussed the various singlet electronic configurations which can be considered for (21) and these are relevant to (23). For the carbene (23) with a carbenic centre approximating sp^3 hybridisation, one electron could reside in the in-plane

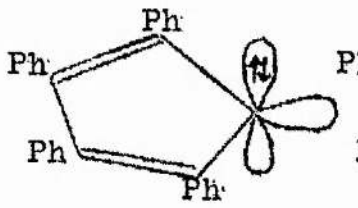
σ-orbital, and the second in the p-orbital (24a); alternatively, both electrons could reside in the σ-orbital (24b); and finally, both electrons could be placed in the p-orbital (24c). The form (24c) is particularly interesting because in this



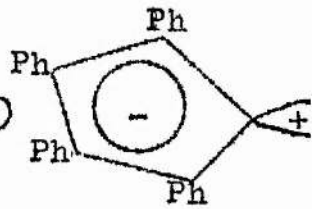
(24a)



(24b)



(24c)



(24d)

system the carbenic pair of electrons should be delocalised over the π-system of the five-membered ring, and thus the carbene could be represented alternatively as (24d). A contribution towards the structure of the carbene (23) from this type of configuration (24d) might lower the energy of the singlet state with respect to the triplet state. A simplified picture of the reaction of the carbene (23) with pyridines and diphenylamine can be got by considering the form (24d) which will be liable to attack from a ternary nitrogen atom with a lone pair of electrons which can occupy the vacant σ-orbital to form a σ-bond. The resulting ylide will be stabilised by electrostatic interaction. Attack by other hetero-atom groups with a lone pair of electrons (e.g. PPh_3) will again involve σ-bond formation. In these cases added stabilisation of the ylide will be afforded by further delocalisation of the

two carbenic electrons in the p-orbital into the available empty d-orbitals of the hetero-atom thus forming a $p\pi - d\pi$ bond.

It thus appears that the thermal decomposition of 2,3,4,5-tetraphenyldiazocyclopentadiene in various compoumds with suitable hetero-atom groups is a general method for the preparation of tetraphenylcyclopentadienylides. One of the limitations of this method is that the hetero-atom reactant must be a liquid at a temperature $>$ ca 120° at normal atmospheric pressure. It is possible that the method could be extended to include low-boiling liquids if the decomposition of the diazo compound was brought about by photolysis. This has not been attempted but during the course of the work some photolytic decomposition experiments involving 2,3,4,5-tetraphenyldiazocyclopentadiene in the presence of hydrocarbonswere reported[121].

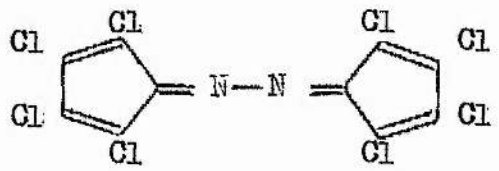
Unfortunately the most important limitation of this method of preparing cyclopentadienylides is that thermal decomposition appears not to be a general reaction. It succeeds in the case of 2,3,4,5-tetraphenyldiazocyclopentadiene and also in the case of 2,5-diphenyldiazocyclopentadiene[92] but it does not succeed for other diazocyclopentadienes (see next section). The requirement would seem to be that a phenyl group must be present in both positions adjacent to the carbenic centre.

2. REACTIONS OF OTHER DIAZOCYCLOPENTADIENES.

(i) Thermal Decomposition

Diazocyclopentadiene was recovered almost quantitatively after it had been heated in refluxing pyridine for twenty-four hours. A little polymeric material had formed but no ylide formation was evident. Diazocyclopentadiene was not heated in a melt owing to its reported explosive nature[143].

When 2,3,4,5-tetrachlorodiazocyclopentadiene was heated above 100° with either triphenylarsine, triphenylstibine, diphenylsulphide or diphenylselenide a very vigorous reaction ensued, clouds of smoke were evolved and a black intractable tar remained in each case. A reaction appeared to take place with pyridine even at room temperature giving a black precipitate. This was insoluble in common organic solvents and resembled a polymeric material which could not be characterised. 2,3,4,5-Tetrachlorodiazocyclopentadiene was unaffected by boiling ethanol but when copper powder was added a high yield of tetrachlorocyclopentadienone azine (25) was obtained. This suggests that a carbenoid intermediate may have been formed



(25)

at the surface of the copper which reacted with a molecule

of the diazo compound at this centre. A similar reaction was reported by McBee et. al.[175] during the course of this work.

2,3,4-Triphenyldiazocyclopentadiene decomposed in refluxing pyridine. Although the infra red spectrum showed the disappearance of the characteristic diazo absorption band no ylide could be isolated from the reaction mixture. The diazo compound decomposed uncontrollably when heated in either triphenylarsine, triphenylstibine, diphenylsulphide or diphenylselenide.

Both 5-chloro- 2,3,4-triphenyldiazocyclopentadiene and 5-bromo-2,3,4-triphenyldiazocyclopentadiene, like 2,3,4-triphenyldiazocyclopentadiene, decomposed uncontrollably when they were each heated with either triphenylarsine, triphenylstibine, diphenylsulphide, or diphenylselenide. In each case no product could be isolated.

All the substituted diazocyclopentadienes mentioned coupled with triphenylphosine to give the respective phosphazine when they were heated together in a melt. These reactions are discussed in the next section.

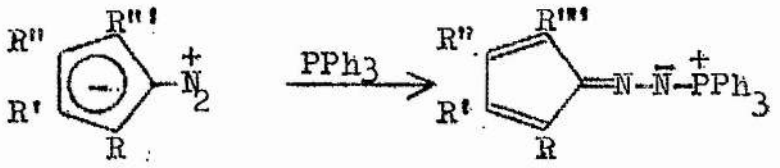
Photolytic decomposition of the diazocyclopentadienes was not attempted but this may well provide a route to other cyclopentadienylides and requires further investigation. A pertinent question which still remains to be answered is, if a carbene intermediate is involved, why the carbene (23) reacts smoothly with hetero-atoms to give ylides whereas

2,3,4-triphenylcarbenacyclopentadiene and other substituted carbenacyclopentadienes appear not to do so.

(ii) Cyclopentadienylidene Phosphazines.

The addition of phosphines generally occurs readily at the terminal nitrogen atom of compounds with the general formula $Y\text{-}\overset{+}{N}\equiv N$. This attack on simple diazonium compounds by trivalent phosphorus is an example of a biphilic process[152], the term 'biphilic' referring to ligands which can donate electrons to a substrate to form a σ-bond and simultaneously accept them at the same centre to form π-bonds. Neutral compounds, $Y\text{-}\overset{-}{N}\text{-}\overset{+}{N}\leftrightarrow Y\text{-}\overset{+}{N}\text{=}N$, also undergo addition reactions with phosphines to give phosphazines. The phosphine reacts at the unsaturated nitrogen and the resultant adduct can be stabilised by back-donation of the nitrogen lone-pair electrons into the vacant 3d-orbitals of phosphorus. Thus the phosphine is behaving both as a nucleophile and electrophile.

Triphenylphosphine coupled readily with 2,3,4-triphenyldiazocyclopentadiene in solution to give the phosphazine (26),



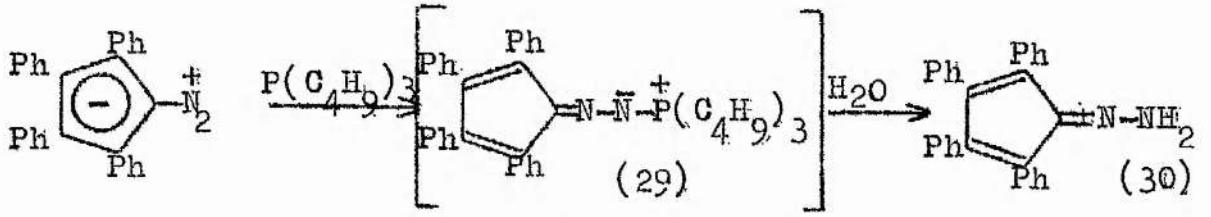
(2.9)

(26) R=H;R'=R"=R"'=Ph
(27) R=Cl;R'=R"=R"'=Ph
(28) R=R'=R"=R"'=Cl

but it was found that 5-chloro-2,3,4-triphenyldiazocyclopenta-

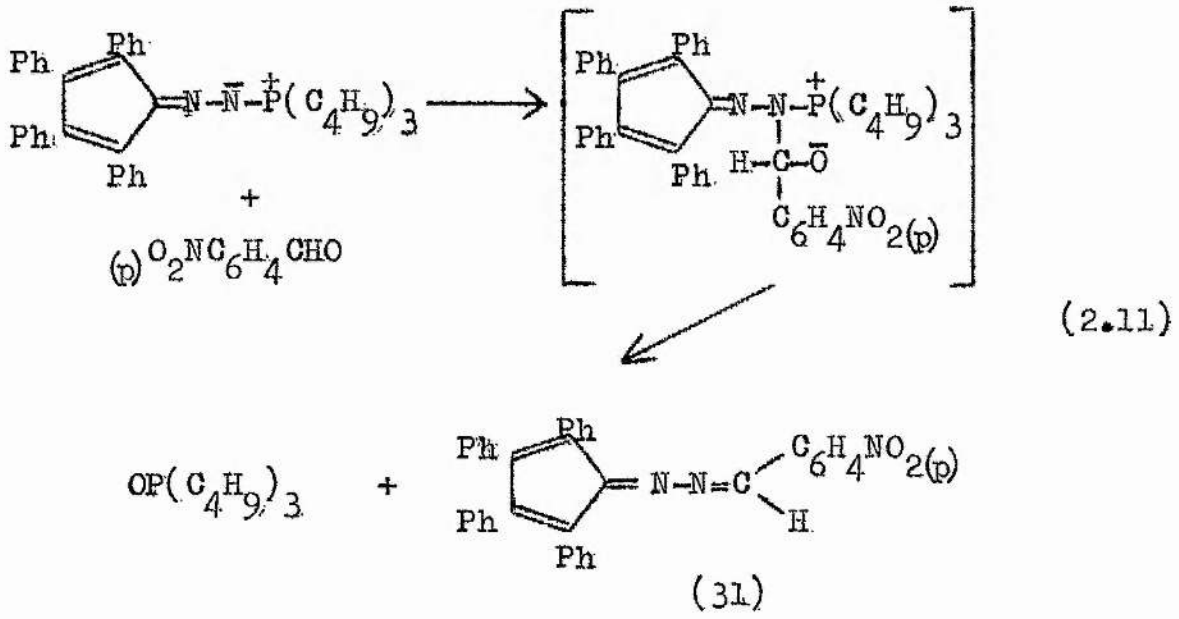
diene only coupled with triphenylphosphine to give (27) under stronger conditions, by heating the reactants in a melt. 5-Bromo-2,3,4-triphenyldiazocyclopentadiene appeared to behave similarly although in this case the adduct was not identified. As previously mentioned (Part II,1,) there was no evidence at all for the formation of a phosphazine when 2,3,4,5-tetraphenyldiazocyclopentadiene was heated in a melt with triphenylphosphine. This suggests that there might be steric hindrance between the approaching phosphine and the phenyl groups at positions 2 and 5 of the five-membered ring. The tetraphenyldiazo compound appeared however to react with the less bulky and more nucleophilic tri-n-butylphosphine to give the phosphazine (29) as an intermediate. It therefore seems likely that the insufficient nucleophilicity of triphenylphosphine together with steric factors inhibited its reaction with 2,3,4,5-tetraphenyldiazocyclopentadiene.

The phosphazine (29) was formed rapidly when the reactants were mixed in warm acetonitrile but it appeared to be readily prone to hydrolysis by moisture from the atmosphere and only 2,3,4,5-tetraphenylcyclopentadienone hydrazone (30) could



(2.10)

be isolated. The hydrazone (30) has not been reported before; it readily undergoes oxidation with mercuric oxide to regenerate the original diazo compound. In an attempt to confirm the presence of (29), tri-n-butylphosphine and the diazo compound were refluxed in dry benzene in the presence of p-nitrobenzaldehyde. A good yield of the azine (31) was isolated which could have been formed by a mechanism analogous



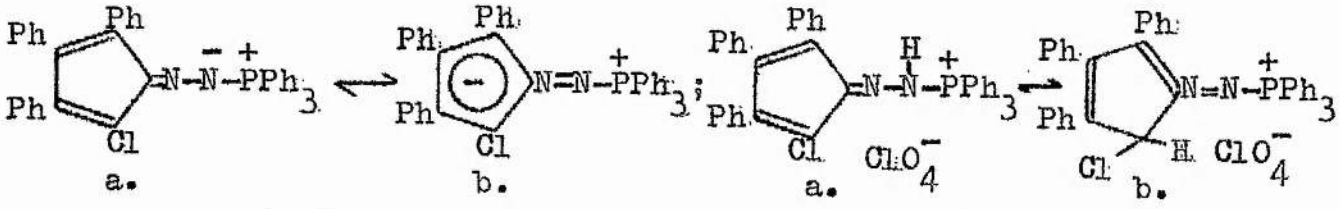
(2.11)

to the Wittig reaction. However the hydrazone (30) also reacted with p-nitrobenzaldehyde in a normal condensation reaction to give (31). Thus although precautions were taken to exclude moisture from the reaction (2.11) it cannot be said with certainty that the intermediate (29) was not first of all hydrolysed to the hydrazone (30) which would then react with p-nitrobenzaldehyde to give the observed product.

2,3,4,5-Tetrachlorocyclopentadienylidenetriphenyl-

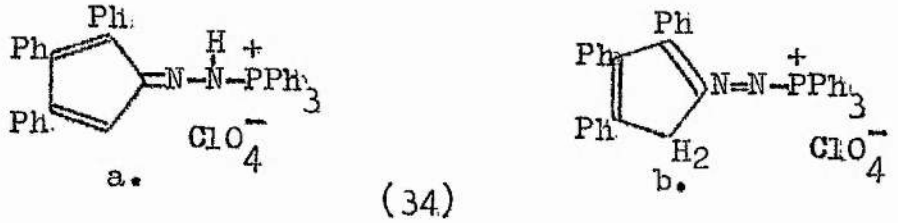
phosphazine (28) had previously been prepared by Disselnkötter[89] who heated 2,3,4,5-tetrachlorodiazocyclopentadiene with triphenylphosphine in solution. It was found that these two reagents coupled when heated together to a melt to give the same compound (28). In general phosphazines are readily hydrolysed and although it has been reported that cyclopentadienylidenetriphenylphosphazine resisted all attempts at hydrolysis[143] it was found that the phosphazine (28) was slowly hydrolysed when exposed to the atmosphere. The hydrolysis products were 2,3,4,5-tetrachlorocyclopentadienone hydrazone and triphenylphosphine oxide. When the phosphazine (28) was heated in the atmosphere at 130° there was a rapid evolution of nitrogen but no tractable material could be isolated from the decomposition products. When (28) was heated under vacuum (0.05mm.) a 35% yield of 2,3,4,5-tetrachlorodiazocyclopentadiene was obtained together with a small amount of the unreacted phosphazine and a trace of a white substance, which from its melting point, was probably triphenylphosphine oxide. Cleavage of the phosphorus - nitrogen bond seemed to have occurred but no triphenylphosphine was detected. The presence of triphenylphosphine oxide indicated that some of the phosphazine was probably hydrolysed from moisture in the atmosphere before reaction had taken place.

Phosphazines are basic and dissolve in dilute mineral acids indicating salt formation. 5-Chloro-2,3,4-triphenylcyclopentadienylidenetriphenylphosphazine (32) was isolated as its perchlorate (33) in order to avoid the possibility of hydrolysis of the base. All the phosphazines which have been



(32) (33)

considered can have an alternative contributing structure (e.g. 32b). Thus there is the possibility that protonation can occur either at the nitrogen atom (e.g. 33a) or at the five-membered ring (e.g. 33b). The I.R. spectrum of (33) showed a typical nitrogen - hydrogen absorption at 3200 cm^{-1} which indicated that protonation occurred on the nitrogen. There was a similar absorption in the I.R. spectrum of the perchlorate (34), and the N.M.R. spectrum of this salt in trifluoroacetic acid showed no peak due to methylene protons as illustrated in (34b). Thus evidence suggests that protonation of substituted cyclopentadienylidenephosphazines takes place at the nitrogen atom.



(34)

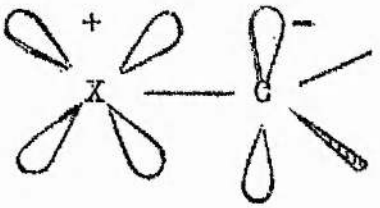
3. PROPERTIES OF TETRAPHENYLCYCLOPENTADIENYLIDES

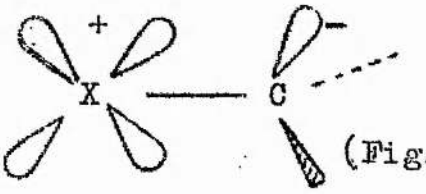
(i) Triphenylphosphonium, triphenylarsonium, and triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylides

a) Structure.-

There are two possibilities for the hybridisation about the carbon atom adjacent to the hetero-atom. These are, trigonal hybridisation with the unshared pair of electrons in a vacant 2p- orbital (Fig.i), and tetrahedral hybridisation with the unshared pair of electrons in a sp^3 hybrid orbital (Fig.ii). No investigation of the hybridisation about the

(Fig.i)





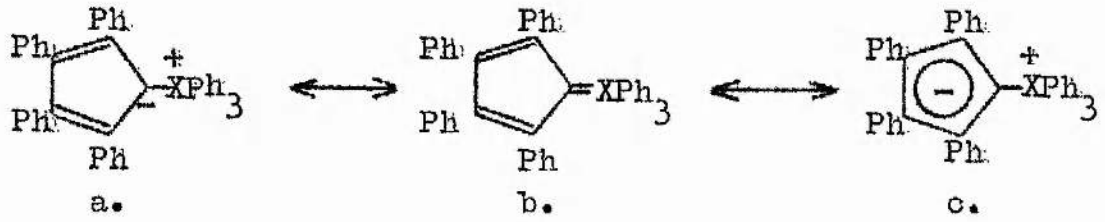
(Fig.ii)

carbon atom in cyclopentadienylides has been made but it seems likely that the carbon atom will adopt a trigonal configuration (Fig.i). In this configuration the delocalisation of the carbanion pair of electrons into the five-membered ring producing a sextet of π-electrons becomes possible whereas this cannot occur if the tetrahedral configuration is adopted. Without this added stabilisation the cyclopentadienylides would certainly lack their characteristic stability.

Very little information is available regarding the hybridisation or geometry of the phosphorus atom in ylides and no corresponding experimental evidence has yet been

reported for the arsenic and antimony atoms. Until X-ray crystallographic work has been done on the ylides (35; X=P,As,Sb) little can be said regarding their actual molecular structure.

The remarkable stability of the cyclopentadienylides has been attributed to the importance of the contribution from the resonance structure (35c), the aromatic cyclopentadienyl form, in which the carbanion pair of electrons is delocalised over the five-membered ring. Delocalisation is also considered



(35) X=P,As,Sb

to occur because of the ability of the hetero-atom (X=P,As,Sb) to expand its valence shell using the vacant, low-energy d-orbitals for overlap with the filled 2p-orbitals in a form of π-bonding. (see Part I, Section 2).

There has been some controversy over the question of the relative ease with which similarly substituted phosphines, arsines, and stibines can undergo valence shell expansion. From a study of triphenylphosphine and triphenylarsine as ligands in metal complexes Chatt and Hart[153] concluded that phosphorus and arsenic have about the same tendency to expand their octets. Similar conclusions were reached from other

studies on metal complexes[154]. Deuterium exchange studies on tetramethyl 'onium salts (36) by Doering and Hoffman suggested that there was little difference in the ability of phosphorus, arsenic, and antimony to expand their valence shells[155].

$$(CH_3)_3\overset{+}{X}-\bar{C}H_2 \longleftrightarrow (CH_3)_3X=CH_2$$

(36)

Johnson[120] has argued that the conclusions reached by Doering and Hoffman were not entirely valid and that valence shell expansion should not necessarily remain constant as group 5A in the Periodic Table is descended from phosphorus to antimony. He agreed that the electrostatic stabilisation of a carbanion by an adjacent 'onium group (X) would be expected to decrease as the Periodic Table is descended since the C-X bond distances increase[155] and the electronegativity of X decreases[156]. In addition, however, and contrary to the

X	C-X Bond distance, Å.	Electronegativity	nd orbital n'
P	1.87	2.1	3
As	1.98	2.0	4
Sb	2.18	1.9	5

(Fig.iii)

conclusions mentioned above he suggests that the stabilisation of a carbanion by an adjacent 'onium atom through overlap of the filled 2p-orbital of the carbanion with a vacant d-orbital of the hetero-atom should decrease down the Table.

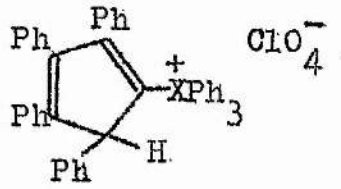
This is expected because the difference between the size of the two atoms involved (carbon-phosphorus, carbon-arsenic, carbon-antimony) becomes larger and the principle quantum number of the d-orbitals used increase (Fig.iii), thereby decreasing the effectiveness of the overlap of the 2p- and nd-orbitals.

The study of the properties and reactions of the presently unique series of ylides (35; X=P, As, Sb) provides some interesting results which can be interpreted in terms of the extent of $p\pi - d\pi$ overlap in the C-X bonding. The problem however is complicated by the possibility of the involvement of steric factors because the C-X bond is surrounded by the bulky phenyl groups which may well influence the reactivity and the course of the reaction of these ylides. In order to draw conclusions from the results it is necessary to assume that steric factors play only a small part in these reactions. If this is taken into consideration then the conclusions reached concerning the $p\pi - d\pi$ bonding are in line with those suggested by Johnson.

b) Physical Properties

The phosphonium ylide (35; X=P) and the arsonium ylide (35; X=As) were yellow crystalline compounds with melting points of 297-299° and 228-230° respectively. The stibonium ylide (35; X=Sb) formed ochre crystals which melted at 196-198° but which could not be recrystallised owing to its ready hydrolysis by moisture both in the solvent and in the atmosphere.

A warm ethanolic solution of the ylide (35; X=Sb) was hydrolysed almost immediately to 2,3,4,5-tetraphenylcyclopentadiene and triphenylstibine oxide. In contrast the phosphonium and arsonium ylides were recovered unchanged after eighteen hours refluxing in alcoholic potassium hydroxide solution. The fact that the arsonium ylide was not hydrolysed indicates the strong stabilising effect of the aromatic five-membered ring, for in general, arsonium ylides are readily hydrolysed in the presence of base. The ylides were insoluble in water, ethanol, and ether but dissolved in benzene and chloroform. They dissolved in dilute mineral acids and with perchloric acid formed yellow crystalline perchlorates (37), presumably

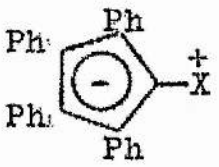


(37) X=P, As, Sb

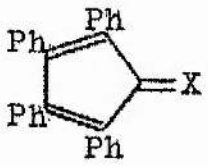
with protonation taking place at the 2-position thereby giving compounds with most conjugation.

The pK_a's of the perchlorates (37) were determined spectroscopically in 95% ethanol solution using the same method as Johnson[82]. Solubility characteristics required the use of this solvent and as a result the pH values of the buffers measured with the pH meter differed from those expected

for aqueous solutions. Therefore the pK_a values determined for the salts are only relative and cannot be compared to values determined in aqueous media. The pK_a of triphenyl-(2,3,4,5-tetraphenylcyclopentadienyl)phosphonium perchlorate (37; X=P) was 5.3 and the corresponding arsonium perchlorate (37; X=As) had a pK_a of 7.6. The pK_a of the stibonium perchlorate (37; X=Sb) could not be determined owing to the very rapid hydrolysis of both the salt and the parent base which took place in 95% ethanol. Rough measurements suggested that the pK_a of (37; X=Sb) was greater than 7.6. These results indicate that the arsonium ylide (39) is more basic than the phosphonium ylide (38) and that the stibonium ylide (40) is more basic than either. This suggests that the



a.



b.

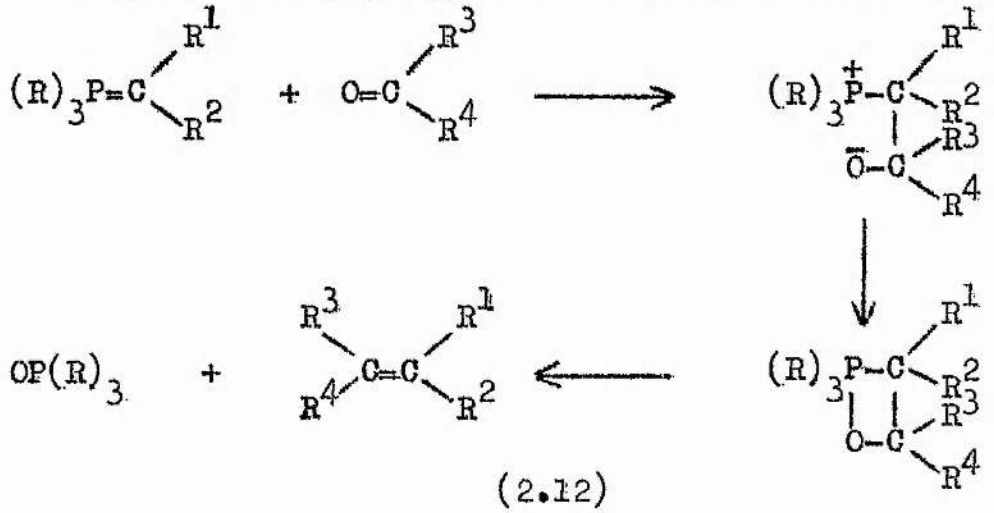
(38) X=P(C_6H_5)$_3$
(39) X=As(C_6H_5)$_3$
(40) X=Sb(C_6H_5)$_3$

amount of stabilisation which the adjacent carbanion recieves by valence shell expansion of the hetero-atom is in the order P > As > Sb. In other words, (40b) contributes less to the overall structure of triphenylstibonium 2,3,4,5-tetraphenyl-cyclopentadienylide than does (39b) to the overall structure of the arsonium ylide which in turn contributes less than does (38b) to the overall structure of the phosphonium ylide (38).

The reactivity of these ylides with carbonyl compounds and with nitrosobenzene, which is now discussed, leads to the same conclusion, although it must be stressed, as mentioned earlier, that possible steric factors are here ignored.

c) Reactions.-

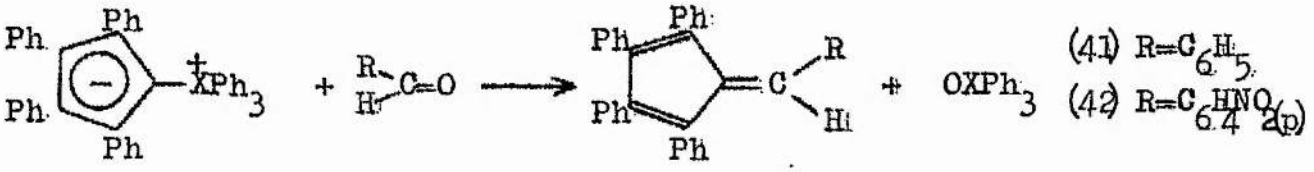
Carbonyl compounds.- The study of a new ylide usually centres on its reaction with carbonyl compounds. This is the well known Wittig reaction and has been studied extensively in the case of phosphonium ylides. The first stage of the reaction is a nucleophilic attack by the ylide on the carbonyl compound to form a phosphonium betaine. Next a P–O bond is formed as a consequence of the affinity of phosphorus for oxygen and its ability to expand its valence shell to ten electrons, giving rise to a four-membered ring intermediate which collapses into a phosphine oxide and an olefin.



(2.12)

Triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide did not react with aldehydes or ketones due to the

reduced nucleophilicity of the ylide. The arsonium ylide (39) reacted with benzaldehyde after refluxing the compounds in carbon tetrachloride for eighteen hours to give a 15% yield of 1,2,3,4,6-pentaphenylfulvene (41). With p-nitrobenzaldehyde

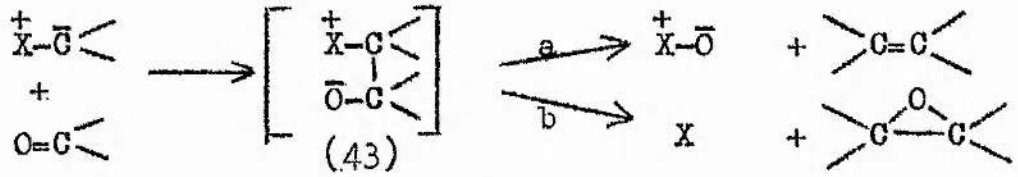


(2.13)

a 95% yield of 6-p-nitrophenyl-1,2,3,4-tetraphenylfulvene (42) was obtained. Under analogous conditions the stibonium ylide (40) gave a 40% yield of the fulvene (41) from benzaldehyde and a 99% yield of the fulvene (42) from p-nitrobenzaldehyde. It was found that carbon tetrachloride was the most convenient solvent to use for these reactions. When chloroform was used for the reaction of the stibonium ylide with aldehydes there was always some 2,3,4,5-tetraphenylcyclopentadiene formed as well. This may be due to hydrolysis from traces of water in the solvent. The arsonium ylide (39) gave similar yields of the fulvene irrespective of whether chloroform or carbon tetrachloride was used as solvent.

It is interesting that in the reaction of the stibonium ylide with aldehydes no fulvene oxide was detected. It might have been expected that the intermediate betaine (43) would follow path b) to give an epoxide (2.14). The only other

reaction of a stibonium ylide with a carbonyl compound was that reported between triphenylstibonium methylide and benzophenone[147] in which triphenylstibine and diphenylacetaldehyde

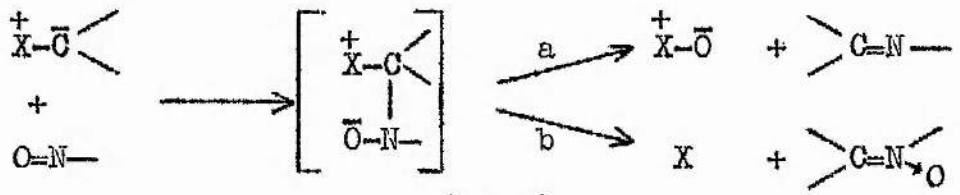


(43)

(2.14)

were formed. The authors suggested that the latter had been formed by rearrangement of an intermediate epoxide (i.e. path b) had been followed). In the reactions under discussion only olefin was isolated suggesting that the driving force to form an antimony - oxygen bond is great enough to direct the course of the reactions along path a) (2.14). The tendency for the formation of a hetero-atom - oxygen bond to control a reaction may account for the products obtained from the reaction of the ylides with nitrosobenzene, discussed next.

Nitrosobenzene.- Nitroso compounds behave in a similar way to carbonyl compounds in their reaction with ylides (2.15), and both triphenylphosphonium- and triphenylarsoniumfluorenylides have been shown to react with nitrosobenzene.

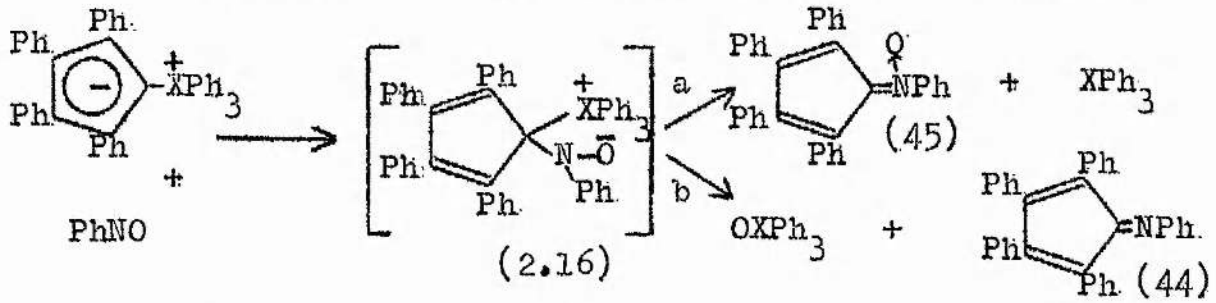


(2.15)

Schonberg and Brosowski[157] found that triphenylphosphonium-

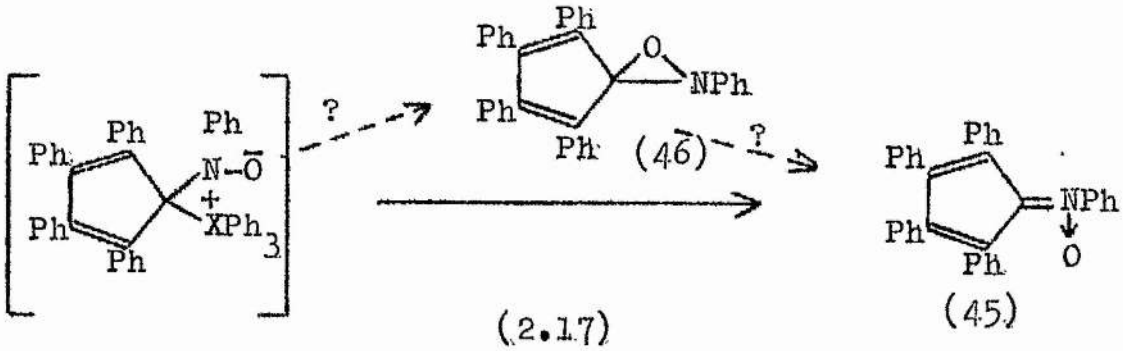
fluorenylide afforded fluorenone anil and triphenylphosphine oxide with nitrosobenzene (i.e. normal Wittig-type reaction with oxygen transfer to phosphorus), whereas Johnson[158] found that triphenylarsoniumfluorenylide and nitrosobenzene gave N-phenyl fluorenone ketoxime and triphenylarsine. This indicates that there is less tendency to form an arsenic - oxygen bond than a phosphorus - oxygen bond.

Triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide (38) had not reacted with nitrosobenzene after these compounds had been heated together in refluxing benzene for eighteen hours. However the arsonium ylide (39) reacted with nitrosobenzene after six hours to afford a 35% yield of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone anil (44), a 10% yield of triphenylarsine oxide, a 48% yield of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (45), and a 33% yield



of triphenylarsine. The stibonium ylide gave only the N-oxide (45) in 81% yield after being heated with nitrosobenzene in boiling benzene for ten minutes; none of the anil (44) could be detected. The mechanism is presumably a Wittig-type in which an intermediate betaine is formed initially (2.16).

This intermediate can then react to follow either path a) or b). If path b) is followed then it might be expected that the oxazirane (46) would be formed, by analogy with epoxide formation. N-Phenyloxaziranes are known to isomerise readily



(2.17) (45)

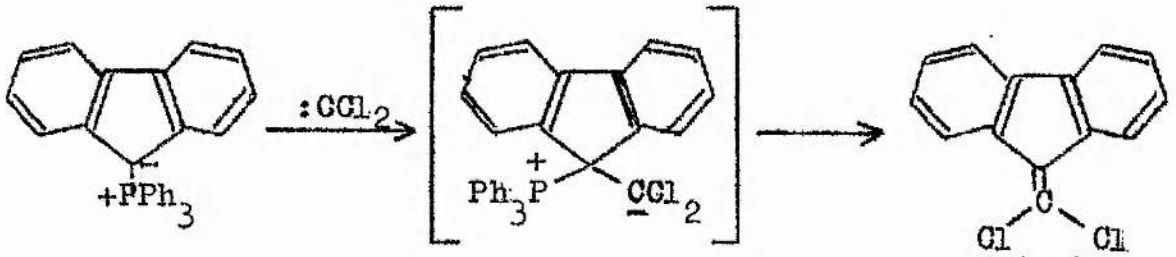
to the corresponding N-oxide[159] and thus if the compound (46) was the initial product isomerisation to the N-oxide (45) can be expected. From the results of the reaction of nitrosobenzene with the tetraphenylcyclopentadienylides it appears that there is less tendency to form an antimony-oxygen bond than an arsenic-oxygen bond, for whereas the arsonium intermediate betaine followed both paths a) and b) to afford a proportion of the anil (44) and triphenylarsine oxide, the stibonium intermediate betaine gave the N-oxide (45) exclusively. The tendency to form a phosphorus-oxygen bond is greater than that to form an arsenic-oxygen bond and if the nucleophilicity of the phosphonium ylide (38) had been strong enough to attack nitrosobenzene initially to form a betaine intermediate it would certainly have followed path a). It appears therefore

that the arsonium ylide (39) holds a position intermediate between the phosphonium ylide (38) and the stibonium ylide (40) in the case of its reaction with nitrosobenzene. The N-oxide (45) was refluxed in benzene with triphenylarsine for twelve hours and was recovered unchanged, thereby confirming that the reaction of the arsonium ylide with nitrosobenzene did not proceed solely to the N-oxide (45), which might then have been reduced to the anil (44) by the triphenylarsine generated in the reaction.

From the reactions of the ylides (38), (39), and (40) with carbonyl compounds and nitrosobenzene it can be deduced that the order of reactivity of the ylides is Sb>As>P. The stibonium ylide is considered to be more reactive than the arsonium ylide because it appeared to undergo its reactions much more readily. The difference in reactions can be attributed to a greater electron density on the carbanion of the stibonium ylide than on the carbanion of the arsonium ylide which in turn has a greater electron density than that on the phosphonium ylide carbanion. This suggests that the delocalisation of the carbanion electrons into the vacant d-orbitals of the hetero-atoms is in the order P>As>Sb, which is consistent with the conclusion reached from a consideration of the basicities of the ylides (iv, this section). This conclusion is also in agreement with that derived by Johnson[83] from a study of the

reactivity and properties of triphenylphosphonium- and triphenylarsoniumfluorenylides but at variance with that reached by Doering and Hoffmann[155], and by Chatt et. al.[153].

Dichlorocarbene: Recently Oda et. al.[160] found that triphenylphosphoniumfluorenylide reacted with chloroform in the presence of tert.-butoxide to afford an olefin (47) and triphenylphosphine. They suggested that the mechanism of the



(2.18) (47)

reaction was the attack by the nucleophilic ylide on dichlorocarbene followed by ejection of the phosphine to afford the olefin (47). The same workers could not effect an analogous reaction with triphenylphosphoniumcyclopentadienylide and they assumed that the failure of the reaction was due to the relative difficulty in localisation of one electron pair on the α-carbon aton (see Part I, Section 2).

In line with these findings the phosphonium ylide (38) did not react with dichlorocarbene. The arsonium ylide (39) was also recovered unchanged after attempted reaction with dichlorocarbene and no olefin could be detected when the stibonium ylide (40) was reacted. This suggests that the

localisation of the electron pairs on the respective α-carbon atoms in all three ylides is insufficient for reaction to take place. Little can be concluded from this lack of reactivity and no deduction can be drawn from this series of experiments concerning the stabilisation of the electron pairs by delocalisation into the d-orbitals of the corresponding hetero-atoms, for it was also found that 2,3,4,5-tetraphenyldiazocyclopentadiene did not react with dichlorocarbene. Presumably the lack of reactivity was again due to the relative difficulty in localisation of the electron pair on the α-carbon atom. In this case delocalisation cannot occur through d-orbital overlap and therefore the aromaticity of the five-membered ring in the diazo compound and the ylides must be a significant cause of their inertness with dichlorocarbene.

(ii) Triphenylbismuthonium 2,3,4,5-tetraphenylcyclopentadienylide.

A discussion of the bismuthonium ylide is strictly limited because there is very little experimental evidence on which to base any conclusions. Whereas the corresponding phosphonium, arsonium, and stibonium ylides were yellow, the bismuthonium analogue (like the corresponding pyridinium ylide) was deep blue. There is a similar difference between pentaphenylantimony, pentaphenylarsenic, and pentaphenylphosphorus which are colourless or yellow, and pentaphenylbismuth which is deep

violet. Also, unlike the phosphonium, arsonium, and stibonium ylides, but like the pyridinium ylides, the bismuthonium ylide gave solutions whose colours varied with the polarity of the solvent; e.g. solutions in benzene or ether were deep blue, in acetone purple-blue, and in methanol red-purple. In methanol the ultraviolet spectrum of the bismuthonium ylide had maxima at λ240, 335, 528 mμ; in benzene maxima at λ280, 345, 596 mμ. These maxima were very similar to those shown by pyridinium 2,3,4,5-tetraphenylcyclopentadienylide in the same solvents.

The bismuthonium ylide was insoluble in dilute and concentrated acids and it decomposed immediately when mixed with them. Solutions of the ylide also rapidly decomposed. Reactions with carbonyl compounds and nitrosobenzene were attempted but no products could be isolated. Thus evidence suggests that the bismuthonium ylide was similar to the pyridinium analogue in its behaviour, i.e. the bismuth atom was behaving more like nitrogen, the first member of the V group, than like antimony which is immediately above bismuth in the Periodic Table. This indicates that there is little if any d-orbital overlap in the ylide and that bismuth cannot readily expand its valence shell.

(iii) Diphenylsulphonium, Methylphenylsulphonium, and Diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylides

Some experimental evidence for suggested $p\pi$-$d\pi$ bonding in sulphonium compounds was mentioned in Part I, Section 2. It is generally agreed that the stabilising effect of a sulphur atom in a ternary sulphonium compound can be attributed to a conjugative electron-accepting mechanism, but it seems to be very difficult to prove that valence shell expansion is involved in this stabilisation. The d-orbital overlap of a sulphonium group with an adjacent carbanion accounts well for sulphonium ylide chemistry and until evidence is provided which cannot be accounted for in this manner the explanation seems justifiable.

Far less is known about ternary selenonium compounds and nothing has previously been known about selenonium ylides. It might be expected that a selenium atom would be able to provide stabilisation to an adjacent carbanion through a similar mechanism to that which operates in ternary sulphonium compounds. The close similarity between diphenylsulphonium and diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylides supports this expectation.

a) Physical Properties.-

Diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (48) and the selenonium analogue (49) were yellow

crystalline compounds with melting points of 216-218° and 189-190° respectively. They appeared to be stable indefinitely at room temperature when exposed to the atmosphere in the absence of light; on exposure to light there was a darkening

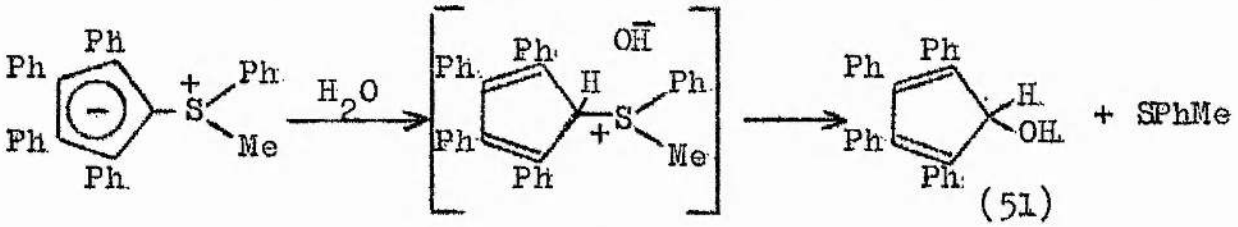
(48) X=S;R=Ph
(50) X=S;R=Me
(49) X=Se;R=Ph

of the crystal surfaces. Their U.V. spectra were similar although the selenonium ylide (49) showed a slight bathochromic shift of the long wavelength band by 11mμ to 302mμ. Both ylides were unaffected by boiling ethanolic sodium hydroxide solution and in each case were recovered unchanged. The ylides (48) and (49) were insoluble in 70% perchloric acid and did not form salts which indicates that they were extremely weak bases. Presumably the pK_a of both ylides is $\ll 5.3$, the value of the corresponding phosphonium ylide (38).

Methylphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (50) was a pale yellow crystalline compound which had m.p. 204-206°. The ylide rapidly darkened on exposure to light but when kept in the dark it appeared to be stable for months. The N.M.R. spectrum of the methylphenylsulphonium ylide (50) in deuteriochloroform showed a complex peak at 2.86τ corresponding to twenty-five phenyl protons, and one

sharp peak at 7.24τ corresponding to three methyl protons. The N.M.R. spectrum of methylphenylsulphide itself in deuteriochloroform included a singlet at 7.67τ due to the methyl protons. The shift of 0.43τ downfield of the signal from the methyl protons in the sulphonium ylide (50) must be due to the deshielding effect of the positively charged sulphur atom.

Hydrolysis of the ylide (50) occurred when it was heated in refluxing ethanolic sodium hydroxide solution for ten hours, but the hydrolysis products could not be isolated. It was expected that normal hydrolysis of the ylide (50) would result in the formation of 2,3,4,5-tetraphenylcyclopentadien-1-ol (51)



(51)

(2.19)

but this compound is unstable in the presence of light and air and it readily decomposes[161]. It is also known to isomerise to 2,3,4,5-tetraphenylcyclopenta-2-en-1-one at high temperatures but this compound was not detected. Thin layer chromatography of the reaction mixture showed that a number of decomposition products had been formed one of which was methylphenylsulphide.

The methylphenylsulphonium ylide (50) was soluble in 70% perchloric acid and gave a bright yellow crystalline perchlorate.

This salt was not very stable and when it was exposed to the atmosphere for about one week it slowly evolved methylphenyl-sulphide. It appeared to be rapidly hydrolysed in aqueous solutions, a yellow ethanolic solution of the perchlorate became colourless after fifteen minutes. The pK_a of the salt could not be determined because of its ready hydrolysis in 95% ethanol but clearly the methylphenylsulphonium ylide (50) was more basic than the diphenylsulphonium and diphenyl-selenonium ylides (48) and (49), which were insoluble in 70% perchloric acid.

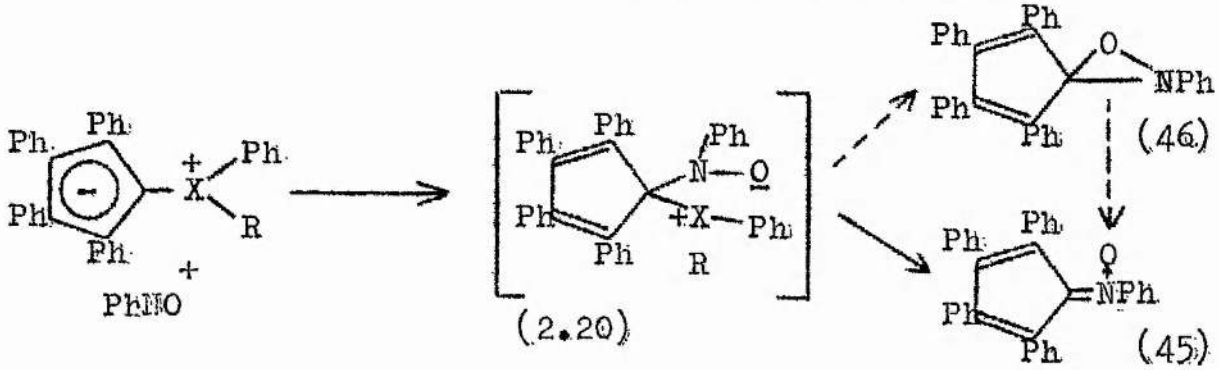
The conclusion that the pK_a of the diphenylsulphonium ylide (48) is less than the pK_a of the methylphenylsulphonium ylide (50) is consistent with a recent report by Johnson and Amel[162] who observed that replacement of a methyl group attached to the hetero-atom of an ylide by a phenyl group led to a decrease in the pK_a of the salt. It is also further evidence to support the proposal that the increase in acidity is due to the powerful inductive withdrawal effect of the phenyl group (relative to the alkyl) which decreases the electron density on the hetero-atom[82]. The lowered electron density on the hetero-atom results in better $p\pi-d\pi$ overlap, which means that in the cases under discussion the diphenyl-sulphonium group affords greater stabilisation to an adjacent carbanion than the methylphenylsulphonium group. This deduction

is supported by the difference in reactivities of the two ylides (48) and (50).

b) Reactions.-

Carbonyl Compounds.- The sulphonium ylides (48) and (50), and the selenonium ylide (49) did not react with aldehydes. They were recovered unchanged after each had been heated to reflux in carbon tetrachloride with 2,6-dinitrobenzaldehyde for twenty hours. As mentioned earlier (i,c, this section) triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide did not react with aldehydes, thus no conclusion can be drawn as to the relative reactivities of these ylides with carbonyl compounds.

Nitrosobenzene.- It was found that the methylphenylsulphonium ylide (50) and the diphenylselenonium ylide (49) reacted with nitrosobenzene after eighteen hours in refluxing benzene to give 81% and 80% yields respectively of the N-oxide (45). Under identical conditions the diphenylsulphonium



ylide (48) gave only a 5% yield of the N-oxide (45). Johnson reacted nitrosobenzene with dimethylsulphoniumfluorenylide[67]

and proposed a reaction course analogous to the reaction shown (2.20). He considered that the reaction might proceed initially through an oxazirane of the type (46), which would immediately isomerise to the observed product (cf 2.17).

(iv) Summary and Comparison of Tetraphenylcyclopentadienylides

It is possible to account for the basicities of the 2,3,4,5-tetraphenylcyclopentadienylides in terms of the relative $p\pi-d\pi$ overlap between the carbanion and its adjacent hetero-atom. Neglecting methylphenylsulphonium 2,3,4,5-tetraphenyl-cyclopentadienylide which carries a different substituent from the other ylides, the order of basicity can be written Sb> As>P >Se≈S. The pK_a's of the diphenylsulphonium and diphenylselenonium ylide conjugate acids are not known but it is probable that, from a consideration of the order of basicities of the Group V ylides, the pK_a of the former will be less than the latter. On the other hand, purely on the basis of their reactions with carbonyl compounds and with nitrosobenzene, a reactivity sequence for the ylides (again neglecting the methylphenylsulphonium ylide) can be written Sb>As>Se>S>P. It is possible to conclude from the sequence of basicities that when the hetero-atoms carry the same substituents the effectiveness of $p\pi-d\pi$ overlap in stabilising the ylides is in the order S>>Se>>P>>As>>Sb.

In Johnson's report on the study of the acidifying effects of 'onium groups in similarly substituted phenacyl 'onium salts[162] nucleophilicity seemed to parallel basicity. The reactivity sequence was based on the reaction of the ylides with carbonyl compounds only. With the series of ylides presently under discussion nucleophilicity does not seem to parallel basicity, and the sulphonium and selenonium ylides were more reactive than the phosphonium ylide, at least in their reactivity with nitrosobenzene. However the all important question of steric effects has been neglected in the discussion and this may well account for some of the apparently anomolous reactivity patterns.

SUMMARY OF REACTIVITY OF TETRAPHENYLCYCLOPENTADIENYLIDES

TABLE I

Reactivity of ylides with aldehydes

Ylide	Hetero-atom group	Yield of fulvene after 18 hr. reaction in CCl_4 at reflux temp.	
		ex benzaldehyde	ex p-nitrobenzaldehyde
(48)	SPh_2	0%	0%
(50)	SPhMe	0%	0%
(49)	$SePh_2$	0%	0%
(38)	PPh_3	0%	0%
(39)	$AsPh_3$	15%	95%
(40)	$SbPh_3$	40%	99%

TABLE II

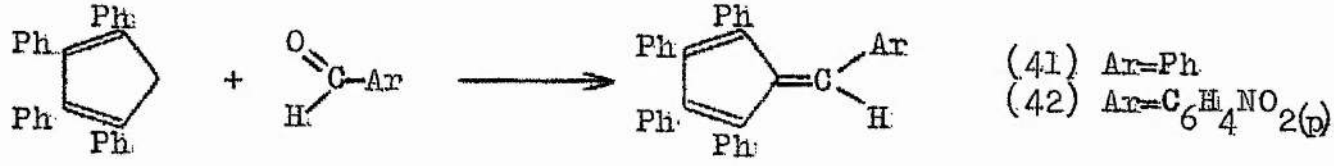
Reactivity of ylides with nitrosobenzene

Ylide	Hetero-atom group	Yield of products from reaction in C_6H_6 at reflux temp.			Reaction time
		N-oxide (45)	Anil (44)	Total (44)+(45)	
(48)	SPh_2	5%	0%	5%	18hr.
(50)	SPhMe	81%	0%	81%	18hr.
(49)	$SePh_2$	80%	0%	80%	18hr.
(38)	PPh_3	0%	0%	0%	18hr.
(39)	$AsPh_3$	48%	35%	83%	4hr.
(40)	$SbPh_3$	80%	0%	80%	10min.

4. PREPARATION OF FULVENES, AND N-PHENYL 2,3,4,5-TETRAPHENYL-CYCLOPENTADIENONE ANIL AND ITS N-OXIDE

(i) Fulvenes

1,2,3,4,6-Pentaphenylfulvene (41) and 6-p-nitrophenyl-1,2,3,4-tetraphenylfulvene (42) were obtained using a similar method to that used by Lowenbein and Ulich[134]. The fulvene (42)

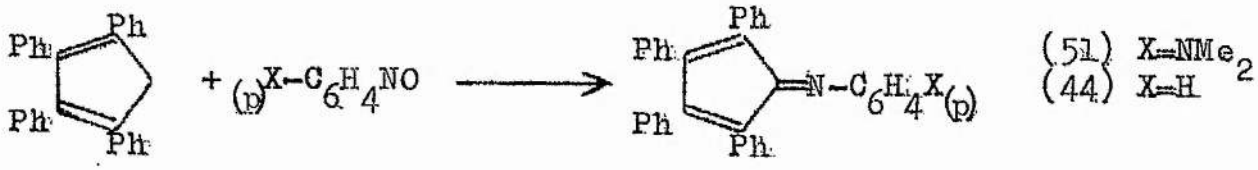


(2.21)

hitherto unreported, was a pale brown crystalline solid with a melting point of 232-234°, and a U.V. spectrum similar to that of the fulvene (41).

(ii) N-Phenyl 2,3,4,5-tetraphenylcyclopentadienone anil

The earliest report of a reaction in which an anil of 2,3,4,5-tetraphenylcyclopentadiene was prepared was by Ziegler and Schnell[172] in 1925. They condensed p-dimethylaminonitrosobenzene with the diene in the presence of sodium ethoxide to



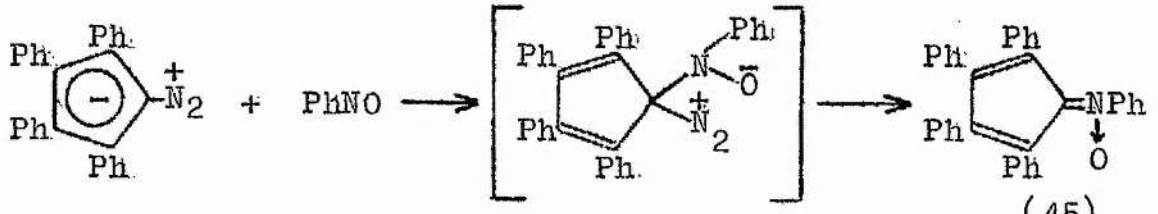
(2.22)

obtain the anil (51) as deep violet almost black crystals. A similar method was used to prepare N-phenyl 2,3,4,5-tetraphenyl-

cyclopentadienone anil (44). This compound was identical to that obtained from the reaction between the arsonium ylide (39) and nitrosobenzene (2.16). It was a deep red crystalline solid , with a U.V. spectrum similar to that of 2,3,4,5-tetraphenylcyclopentadienone.

(iii) N-Phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime

As early as 1919 Staudinger and Mischer[66] found that diazofluorene and nitrosobenzene underwent a reaction at room temperature to afford N-phenyl fluorenone ketoxime. A similar method was adopted, although a higher temperature was necessary, to prepare N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (45). It was a khaki-green solid, m.p. 224-226°,

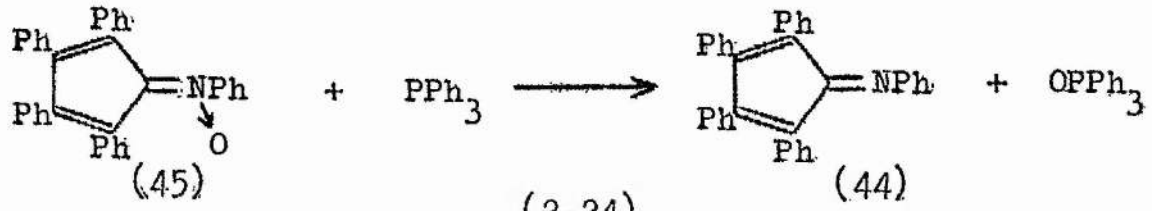


(2.23) (45)

whose I.R. spectrum showed two strong absorption bands at 1290 cm^{-1} and 898 cm^{-1} respectively, characteristic of the vibrational modes due to the N-O linkage in aromatic amine oxides[173].

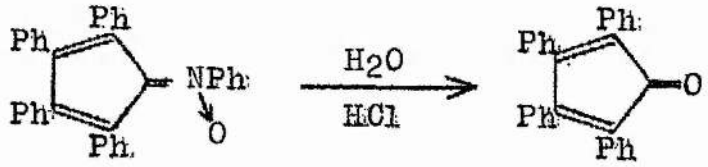
An attempt was made to prepare the N-oxide (45) by oxidising the anil (44) but neither of the two reagents tried, perphthalic acid, and hydrogen peroxide in the presence of glacial acetic acid, was effective. However the N-oxide was

successfully reduced to the anil (44) using a boiling solution



(45) (2.24) (44)

of triphenylphosphine in benzene (2.24). Attempted reduction using phosphorus trichloride did not lead to the anil, but addition of water to the reaction mixture gave 2,3,4,5-tetraphenylcyclopentadienone as one of the hydrolysis products (2.25).



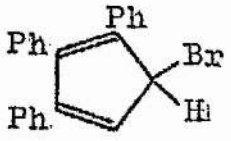
(45) (2.25)

5. PREPARATION OF PYRIDINIUM AND TRIPHENYLPHOSPHONIUM TRIPHENYL-CYCLOPENTADIENYLIDES.

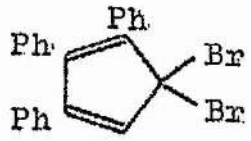
(i) 5-Bromo-2,3,4-triphenylcyclopentadiene.

The method used to prepare 2,3,4,5-tetraphenylcyclopentadienylides by the decomposition of the corresponding diazo compound was found to be unsuccessful for the preparation of 2,3,4-triphenylcyclopentadienylides.

The most common method of preparing ylides is the basification of an 'onium salt initially formed by alkylation of the appropiate base. The preparation of 5-bromo-2,3,4-triphenylcyclopentadiene (52) was described in the literature by Pauson and Williams[135]. This consisted of treating 2,3,4-triphenylcyclopentadiene with a one molar equivalent of bromine in carbon disulphide at room temperature and leaving the mixture for twenty-four hours. These workers reported that the use of N-bromosuccinimide or of two molar equivalents of bromine afforded the 5,5-dibromo compound (53). It has been



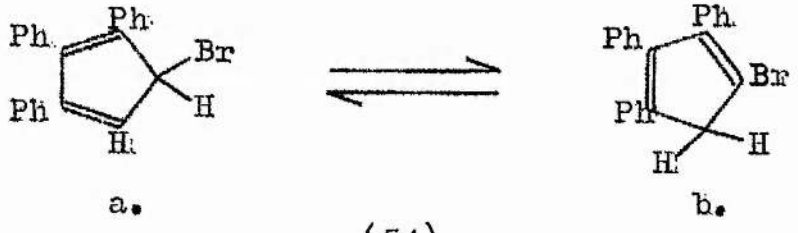
(52)



(53)

found however that monobromination of 2,3,4-triphenylcyclopentadiene can be effected using N-bromosuccinimide. A slight

molar excess of the diene in carbon tetrachloride was heated to reflux for forty-five minutes with N-bromosuccinimide and a good yield of the bromo compound (52) was obtained with no contamination from the dibromo compound (53). When the work of Pauson and Williams was repeated using bromine as the brominating agent the monobromo compound could not be obtained free from the dibromo compound. An examination of the N.M.R. spectrum of a pure sample of the monobromo compound (52) suggested that it exists as a mixture of tautomers (54).



a. b.

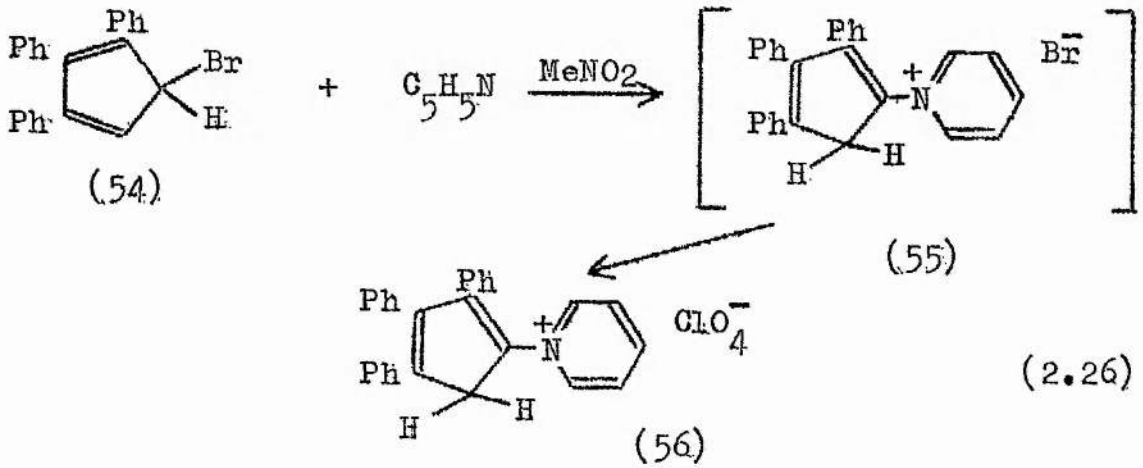
(54)

The spectrum showed one singlet at 6.2τ which would correspond to the methylene group in (54b) (cf. 6.0τ for the methylene group in 2,3,4-triphenylcyclopentadiene) and two doublets, one centred at 3.5τ, and the other centred at 4.4τ. These would correspond to the two single protons shown in (54a). The splitting of the doublet was small (2 c/s) and this may be explained by the fact that the two protons will be almost at right angles to each other due to the presence of the large bromine atom which will tend to push the adjacent proton more out of the plane of the five-membered ring.

The existence of the tautomer (54b) with an active methylene group could explain the readiness with which the monobromo compound undergoes further bromination.

(ii) Pyridinium 2,3,4-triphenylcyclopentadienylide

The method by which Lloyd and Sneezum[94] prepared N-(2,3,4,5-tetraphenylcyclopentadienyl)pyridinium bromide (see Part II,1) was first of all used in an attempt to obtain N-(2,3,4-triphenylcyclopentadienyl)pyridinium bromide (55). The monobromo compound (54) was left in an excess of pyridine for twelve hours and although the solution became deep red indicating that some reaction had taken place there was no precipitate of the expected bromide salt (55). This salt was prepared, as an intermediate, by heating equimolar amounts of pyridine and the monobromo compound (54) at 90° in nitromethane for two hours (2.26). During the work-up perchloric acid was added



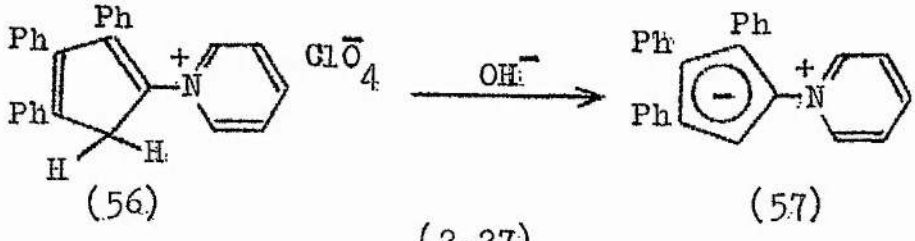
(2.26)

and the perchlorate (56) was isolated instead of the bromide since perchlorates are generally more highly crystalline and

less likely to be hygroscopic than the corresponding bromides.

The perchlorate (56) was an orange crystalline solid with an N.M.R. spectrum in trifluoroacetic acid which showed complex multiplets between 1.2τ and 2,8τ due to the pyridinium and phenyl protons, and a sharp singlet at 5.6τ corresponding to a methylene group. The presence of a methylene group in the perchlorate (56) confirms that the alkylation of pyridine (2.26) involved a prototropic shift to give the more stable system with a longer conjugated chain.

The salt (56) was hydrolysed in ethanol and aqueous sodium hydroxide to give pyridinium 2,3,4-triphenylcyclopentadienylide (57).

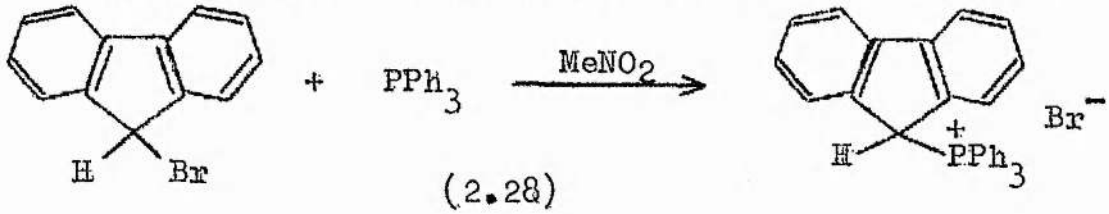


(56) (57)

(2.27)

(iii) Triphenylphosphonium 2,3,4-triphenylcyclopentadienylide

Pinck and Hilbert[76] prepared and isolated triphenylphosphoniumfluorenylide by addition of triphenylphosphine to



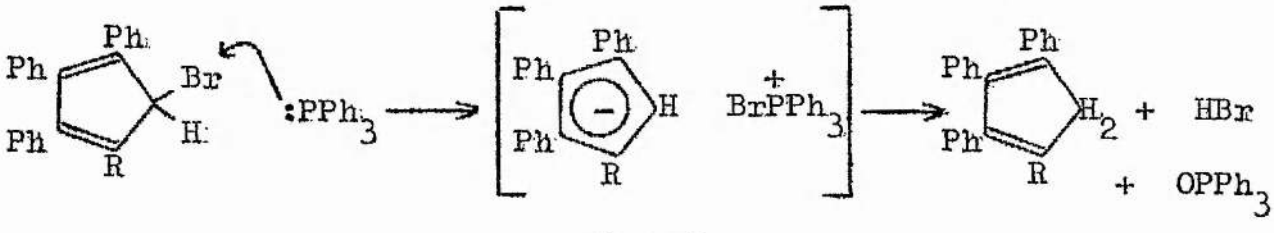
(2.28)

a solution of 9-bromofluorene in nitromethane to give the phosphonium bromide in good yield (2.28), which they isolated

and subsequently basified to obtain the phosphonium ylide. When the same method (2.28) was used in an attempt to prepare triphenyl(2,3,4-triphenylcyclopentadienyl)phosphonium bromide (60) from 5-bromo-2,3,4-triphenylcyclopentadiene and triphenylphosphine none of the expected salt was formed but a high yield of 2,3,4-triphenylcyclopentadiene (58) was obtained.

(2.29)

It appears that the triphenylphosphine in nitromethane reduced the bromo compound (54) to the diene (58). An identical reaction occurred when triphenylphosphine was added to a solution of 5-bromo-1,2,3,4-tetraphenylcyclopentadiene in nitromethane and 2,3,4,5-tetraphenylcyclopentadiene (59) was obtained. The mechanism proposed for the reaction is as follows:

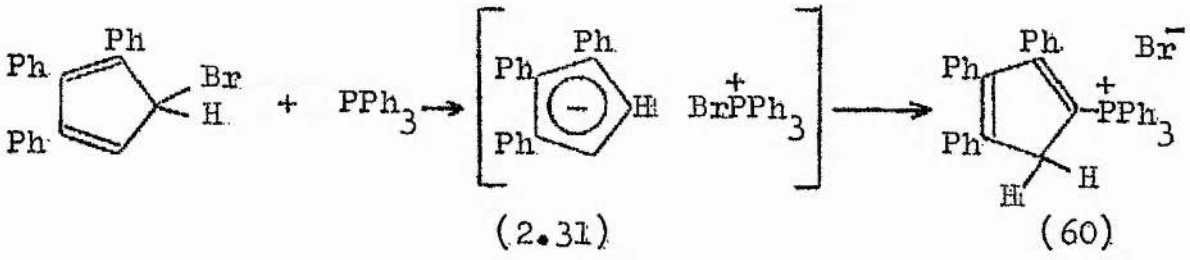


(2.30)

The triphenylphosphine attacked the electrophilic bromine atom and displaced the aromatic cyclopentadienyl anion which then reacted with traces of water in the solvent or possibly with a proton from nitromethane to give the observed diene.

It is known that tertiary phosphines in hydroxylic solvents will attack a positively polarised halogen of an organic compound resulting in reductive elimination of the halogen[163]. In this case the electron-withdrawing effect of the five-membered ring will tend to polarise the carbon - bromine bond, thus giving the bromine atom a partial positive charge, and the carbanion remaining after removal of the bromonium ion will be stabilised by delocalisation of the charge over the five-membered ring. Water may have been present in small amounts in the nitromethane and this would be rapidly attacked by the cyclopentadienyl anion. Nitromethane itself, with an acidic proton, may also be liable to attack from the anion. The reason that this type of reaction (2.30) did not occur in the case of 9-bromofluorene may be explained in terms of the relative tendency of the two systems, fluorene and cyclopentadiene, to lose a proton to form an aromatic system. The pK_a of cyclopentadiene is 15 compared to 23 for fluorene and this suggests a greater driving force to form the aromatic cyclopentadienyl system than that to form the corresponding fluorenyl system. This means that whereas attack on 9-bromofluorene by triphenylphosphine occurs at the carbon atom with simple displacement of the bromide ion, the bromocyclopentadienes (58) and (59) will be more liable to attack at the bromine atom.

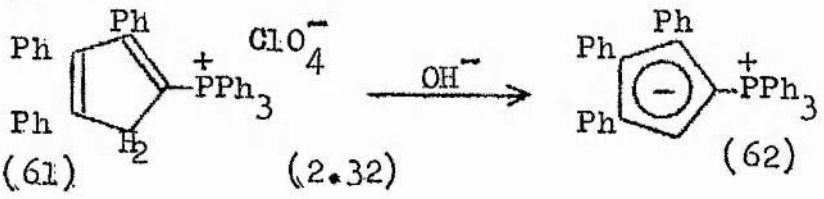
It therefore appeared that if the reaction of 5-bromo-2,3,4-triphenylcyclopentadiene with triphenylphosphine was carried out in the absence of a proton-supplying solvent the only path open to the displaced anion would be attack at the phosphonium centre to produce the phosphonium bromide (60). It was found that no solvent was necessary. A mixture of the two reactants, with an excess of triphenylphosphine, was heated at 150° and an almost quantitative yield of the bromide (60)



(2.31) (60)

was obtained. The reaction (2.31) is again considered to proceed through the cyclopentadienyl anion which, in the absence of any other electrophile, attacked $Br\overset{+}{P}Ph_3$. A similar reaction occurred between the bromo compound (59) and triphenylphosphine.

The bromide (60) was converted into the crystalline perchlorate (61), whose N.M.R. spectrum was consistent with the structure (61), showing a complex multiplet centred at 2.5τ and a singlet at 5.88τ. Triphenylphosphonium 2,3,4-triphenyl-cyclopentadienylide (62) was prepared by hydrolysis of the perchlorate (61).

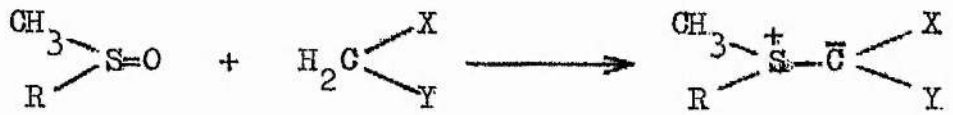


(61) (2.32) (62)

6. PREPARATION OF TRIPHENYLARSONIUM 2,3,4-TRIPHENYLCYCLOPENTADIENYLIDES

The method used for the preparation of triphenylphosphonium 2,3,4-triphenylcyclopentadienylide (62) did not appear to be successful for the preparation of the corresponding arsonium ylide, and 5-bromo-2,3,4-triphenylcyclopentadiene also failed to react with triphenylarsine when the two compounds were boiled in nitromethane for six hours.

A number of reports have recently appeared in the literature concerning the preparation of sulphonium ylides by condensation of sulphoxides with compounds containing an active methylene group. Nozaki *et al.*[164] reacted dimethylsulphoxide



(2.33)

and methylphenylsulphoxide with methylene compounds (2.33) in which the substituents X and Y were either keto, ester, or nitrile groups. The reactions were effected either by heating the reaction components in acetic anhydride solution under reflux for twenty hours, or by heating a triethylamine solution of both reactants at 100° for five hours in the presence of phosphorus pentoxide. A search of the literature showed that no related reaction had been carried out with an arsine oxide and an active methylene compound, although Horner and Oediger[165]

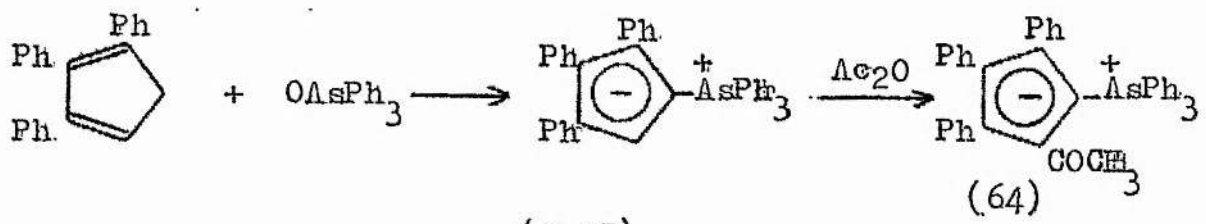
have reacted triphenylarsine dichloride with active methylene compcunds to afford stabilised arsonium ylides.

A solution of 2,3,4-triphenylcyclopentadiene and triphenylarsine oxide in triethylamine was heated to reflux for twenty-four hours with phosphorus pentoxide added (2.34).

(63)

(2.34)

This was found to be a successful method for the preparation of triphenylarsonium 2,3,4-triphenylcyclopentadienylide (63) which was obtained in 55% yield[166]. When a solution of 2,3,4-triphenylcyclopentadiene and triphenylarsine oxide in acetic anhydride was heated to reflux for ten minutes a 70% yield of



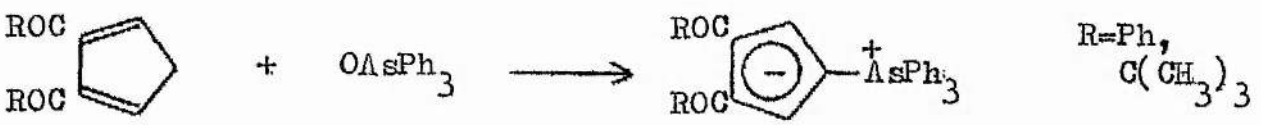
(64)

(2.35)

triphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylide (64) was isolated[166]. Presumably the arsonium ylide (63) was initially formed and then rapidly acetylated by the acetic anhydride. The arsonium ylide (63) has been shown to undergo acetylation readily (Part II,7,ii).

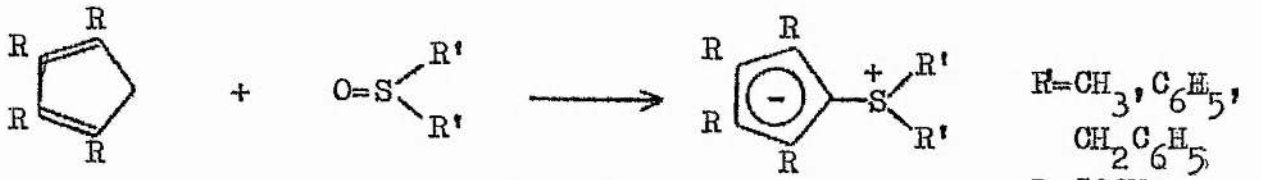
The attempted preparation of triphenylarsonium 2,3,4,5-

tetraphenylcyclopentadienylide (39) using either triethylamine and phosphorus pentoxide or acetic anhydride failed suggesting that in this case steric hindrance inhibited the reaction between 2,3,4,5-tetraphenylcyclopentadiene and triphenylarsine oxide. However it has been found that both dibenzoylcyclopentadiene and dipivaloylcyclopentadiene condense readily with triphenylarsine oxide in warm acetic anhydride to give the corresponding ylides[166,167]. In this instance acetylation



(2.36)

did not occur owing to the deactivation of the five-membered ring caused by the presence of the two electron-withdrawing acyl groups. During the course of this work Seitz[168] reported some related reactions in which sulphonium cyclopentadienylides were formed. This consisted of mixing 2,3,4,5-tetracarbomethoxycyclopentadiene with a sulphoxide in acetic anhydride at room temperature and after a few hours the corresponding sulphonium ylide could be isolated.



(2.37)

7. PROPERTIES OF TRIPHENYLCYCLOPENTADIENYLIDES.

(i) Pyridinium 2,3,4-triphenylcyclopentadienylide

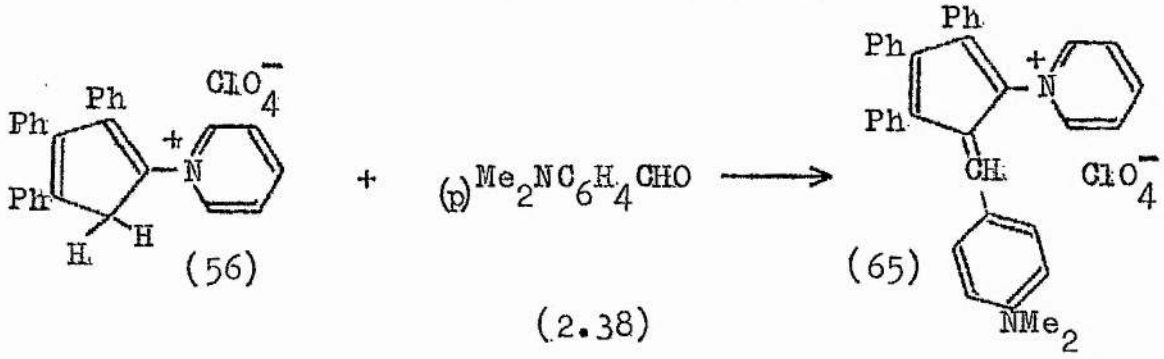
a) Physical Properties.

The pyridinium ylide (57) was a purple solid, melting at 183-186°, which appeared to be stable for months but in solution it decomposed rapidly. Like the tetraphenyl analogue[94] (1) it could not be recrystallised from any of the common organic solvents and attempted chromatography resulted in immediate decomposition of the ylide. However a sample of the pyridinium ylide (57) prepared from the perchlorate (56), under dust-free conditions, gave elemental analysis figures which were consistent with those for the proposed structure. The colours of the solutions of pyridinium 2,3,4-triphenylcyclopentadienylide, like those of the other pyridinium cyclopentadienylides, varied with the polarity of the solvents e.g. in benzene and ether its solutions were blue and in methanol its solution was orange. The U.V. spectrum of the ylide was similar to that of the tetraphenylcyclopentadienylide and it showed a bathochromic shift of the long wavelength band of 52mμ from methanol to benzene.

b) Reactions of N-(2,3,4-triphenylcyclopentadienyl)-pyridinium perchlorate.

p-Dimethylaminobenzaldehyde. The pyridinium perchlorate (57) can be considered as a substituted cyclopentadiene and

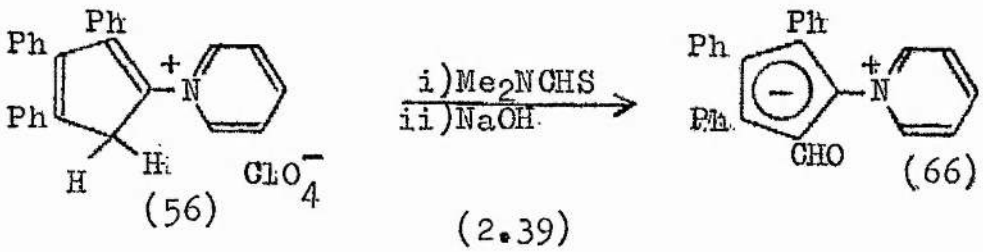
therefore would be expected to have an active methylene group, especially since this group is conjugated with a positively charged centre. This reactivity was confirmed by its ready condensation with p-dimethylaminobenzaldehyde to give a



(56) (2.38) (65)

p-dimethylaminobenzylidene derivative (65). This was a highly coloured crystalline salt which was protonated in acid solution to give a yellow dication.

Formylation. Since the pyridinium ylide (57) tended to decompose in solution a formylation procedure was adopted which involved the use of the perchlorate (56). A modified version of the Vilsmeier reaction developed by Dingwall and Reid[169] was found to give a good yield of pyridinium 5-formyl-2,3,4-triphenylcyclopentadienylide (66), a bright orange-red compound which, in contrast to the unsubstituted triphenyl-



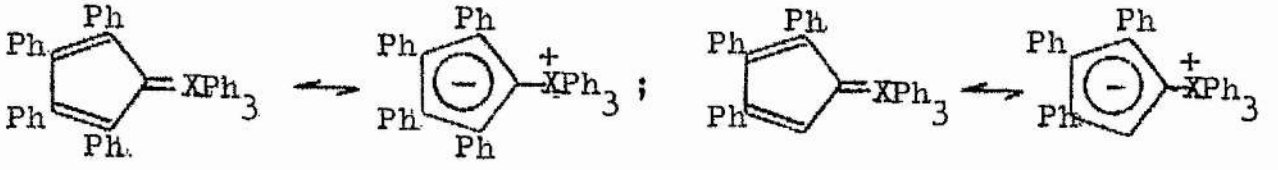
(56) (2.39) (66)

cyclopentadienylide (57), could be chromatographed and recrystallised. The stability of the formyl compound (66) arises from the electron-withdrawing effect of the formyl group which further delocalises the negative charge.. Its I.R. spectrum showed a carbonyl absorption at 1615 cm^{-1} which indicates considerable polarisation of the carbon-oxygen double bond, and its U.V. spectrum showed a bathochromic shift of the long wavelength absorption by 80 mμ from methanol to benzene suggesting a highly dipolar ground state. The N.M.R. spectrum in deuteriochloroform showed a complex multiplet centred at 2.3τ and a sharp singlet at 0.50τ due to the formyl proton.

(ii) Triphenylphosphonium and Triphenylarsonium 2,3,4-triphenyl-cyclopentadienylides.

a) Physical Properties.

Both the triphenylphosphonium and triphenylarsonium ylides (62) and (63) were pale yellow crystalline compounds which melted at 259-261° and 198-200° respectively. They appeared to be stable indefinitely and were recovered unchanged after each had been boiled in ethanolic sodium hydroxide solution for eighteen hours. Their U.V. spectra were almost identical with those of the corresponding tetraphenyl analogues (38) and (39). The ylides (62) and (63) were soluble in dilute mineral acids and were characterised as the yellow

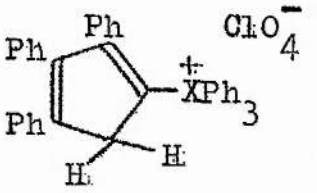


a. b. a. b.

(38) X=P (62) X=P

(39) X=As (63) X=As

crystalline perchlorates (61) and (64) respectively. The N.M.R. spectra of the salts were consistent with the structure shown, and further evidence for the presence of a methylene group was obtained by reacting each perchlorate with p-dimethyl-

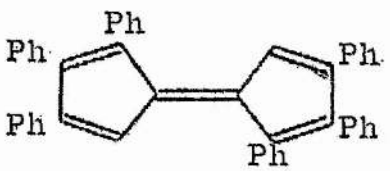


(61) X=P

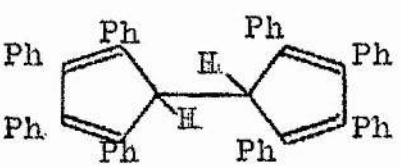
(64) X=As

aminobenzaldehyde to form a p-dimethylaminobenzylidene derivative (cf. reaction (2.38)). The pK_a's of the perchlorates (61) and (64), determined in 95% ethanol, were 4.2 and 6.6 respectively. This indicates that the arsonium ylide (63) was more basic than the phosphonium ylide (62) and is exactly analogous to the tetraphenylcyclopentadienylide system (see Part II, 3, i). In other words, (62b) contributes less to the overall structure of triphenylphosphonium 2,3,4-triphenyl-cyclopentadienylide than does (63b) to the overall structure

of the arsonium ylide (63). The lower pK_a values of the 2,3,4-triphenylcyclopentadienylides compared with those for the corresponding 2,3,4,5-tetraphenylcyclopentadienylides similarly indicates a greater contribution from the non-polar form in the case of the 2,3,4-triphenylcyclopentadienylides and may be rationalised in terms of steric effects. Interaction of the exocyclic phenyl groups with the phenyl groups at positions 2 and 5 of the five-membered ring in the tetraphenylcyclopentadienylides will tend to reduce the double bond nature of the C-X bond, resulting in more dipolar character. This interaction will be less in the case of the triphenylcyclopentadienylides in which there is only one adjacent phenyl group on the five-membered ring and thus greater double bond character of the C-X linkage is possible. The failure by Pauson and Williams[170] to prepare octaphenylfulvalene was attributed to a similar but far more evident steric interaction. Whereas 2,3,4,2',3',4'-hexaphenylfulvalene (67) was readily isolated and considered to exist as a relatively unhindered (and probably near-planar) trans-isomer, the



(67)

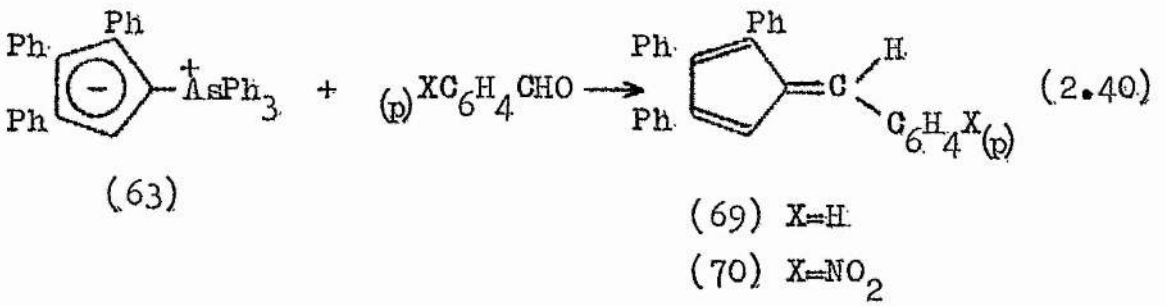


(68)

attempted preparation of octaphenylfulvalene always resulted in the formation of the dihydro derivative (68). These workers concluded that their inability to introduce a 1,1'-double bond into (68) was due to the steric overcrowding of the 2,5,2',5'-substituents which made coplanarity impossible.

b) Reactions.

Carbonyl Compounds. Like its tetraphenyl analogue triphenylphosphonium 2,3,4-triphenylcyclopentadienylide (62) did not react with carbonyl compounds. The arsonium ylide (63) reacted with both benzaldehyde and p-nitrobenzaldehyde to give fulvenes in 35% and 90% yields respectively.

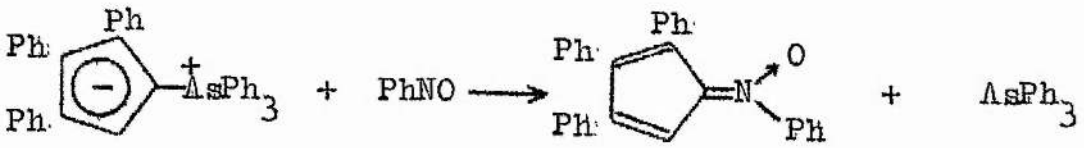


(63) (69) X=H (70) X=NO_2 (2.40)

The reactivity of the two ylides (62) and (63) with carbonyl compounds indicates that their nucleophilicity parallels their basicity, as was also found for the tetraphenyl analogues (38) and (39). However in the case of the two arsonium ylides (39) and (63), the ylide (63) had a lower pK_a and would therefore be expected to be less reactive towards electrophiles, yet it was slightly more reactive towards benzaldehyde. This apparent contradiction may be due to a lower steric inhibition in the

triphenylcyclopentadienylide (63).

Nitrosobenzene. The phosphonium ylide (62) had not reacted with nitrosobenzene after the reactants had been refluxed in benzene for eighteen hours. Under the same conditions the arsonium ylide (63) gave a 15% yield of N-phenyl-2,3,4-triphenylcyclopentadienone ketoxime (71). This was a lower yield than was obtained from the corresponding



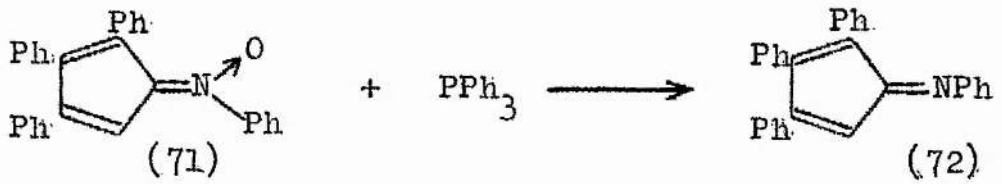
(63) (71)

(2.41)

reaction of the tetraphenyl analogue (2.15) and correlates with the lower basicity of the ylide (63). N-Phenyl 2,3,4-triphenylcyclopentadienone anil (72) was not detected in the reaction (2.41). Although 2,3,4-triphenylcyclopentadienone has been prepared as a stable monomer[171] most trisubstituted cyclopentadienones exist as dimers. However the anil (72) could not have been formed and then lost by dimerisation since it was shown to be stable under the reaction conditions.

The N-oxide (71) was also prepared from 2,3,4-triphenyldiazocyclopentadiene and nitrosobenzene (cf. 2.23) and its properties were very similar to those of the tetraphenyl analogue (45). Reduction of the N-oxide (71) was effected

using triphenylphosphine to give N-phenyl 2,3,4-triphenyl-cyclopentadienone anil (72) which had been prepared alternatively

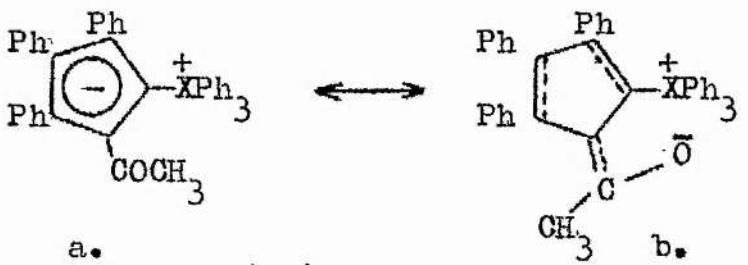


(71) (72)

(2.42)

by condensation of 2,3,4-triphenylcyclopentadiene with nitrosobenzene. The anil (72) was a stable highly crystalline monomer which showed no tendency to dimerise. Its U.V. spectrum was similar to that of 2,3,4,5-tetraphenylcyclopentadienone except for a hypsochromic shift of the long wavelength absorption by 39mμ.

Electrophilic Substitution. Cyclopentadienylides, by virtue of the high charge density on the five-membered ring, are prone to electrophilic attack (see Part I, Section 2). Acetylation of triphenylphosphonium and triphenylarsonium 2,3,4-triphenylcyclopentadienylides took place readily when each ylide was heated to reflux in acetic anhydride. The carbon-oxygen bond in both acetyl compounds (73; X=P,As)



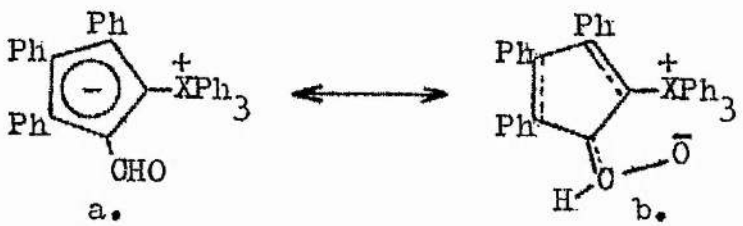
a. b.

(73) X=P,As

appeared to be highly polarised. The I.R. spectrum of each compound did not show carbonyl absorption above 1600 cm^{-1} and below this value it was difficult to interpret the spectra owing to the presence of absorption due to the phenyl groups. It seems probable that in each case the close proximity of the positively charged hetero-atom will encourage polarisation of the carbon-oxygen bond further. The U.V. spectra of the two acetyl compounds (73; X = P, As) were almost identical and their N.M.R. spectra showed a complex multiplet centred at 2.7τ and a sharp singlet at 8.2τ corresponding to a methyl group. As a result of the increased delocalisation of the negative charge into the carbonyl group, triphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylide (73; X=As) had not reacted with 2,6-dinitrobenzaldehyde after the reactants had been heated to reflux in carbon tetrachloride for twenty-four hours.

Formylation of the triphenylphosphonium and triphenylarsonium 2,3,4-triphenylcyclopentadienylides was effected with phosphorus oxychloride in dimethylformamide and subsequent basification. The resultant 5-formyl compounds (74; X=P,As), and their perchlorates, had elemental analysis figures which were consistent with the proposed structures, but their N.M.R. spectra in both deuteriochloroform and trifluoroacetic acid showed only a complex multiplet centred at 2.8τ with no

signal corresponding to an aldehyde proton. An explanation for this behaviour is that a large contribution from a



(74) X=P,As

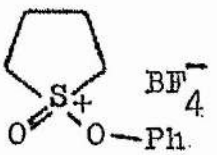
resonance form of the type (74b) is again responsible. The formyl group will gain a high degree of negative charge from the five-membered ring resulting in a highly polarised carbon-oxygen bond, and the exocyclic carbon-carbon linkage will assume more double bond character. This will tend to produce a more rigid structure with the correct geometry for maximum interaction between the oxygen atom and the positively charged hetero-atom. The single proton will thus be in a different environment from that of a normal aldehyde proton and this may result in a reduction of the deshielding normally associated with the carbonyl bond. The N.M.R. signal of this proton could therefore appear in the region 2.2-3.5τ and consequently be hidden under the complex multiplet due to the phenyl protons. The I.R. spectra of the two formyl compounds (74; X=P,As), which were almost identical, did not show a normal carbonyl absorption. The only absorption in the carbonyl region was one at 1600 cm^{-1} but this absorption was

also present in the spectra of the unformylated compounds and was attributed to the phenyl groups. It appears that in these formyl compounds (74; X=P,As) there is an interesting intramolecular electrostatic effect which requires further investigation.

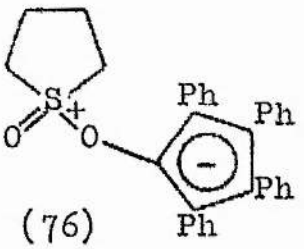
8. MISCELLANEOUS REACTIONS

(i) Reaction between 2,3,4,5-Tetraphenyldiazocyclopentadiene and Tetrahydrothiophene-1,1-dioxide

Whiting[174] reported the isolation of a crystalline salt (75) and it was thought that the structurally similar pseudo-ylide (76) might be isolable. However when 2,3,4,5-tetraphenyl-

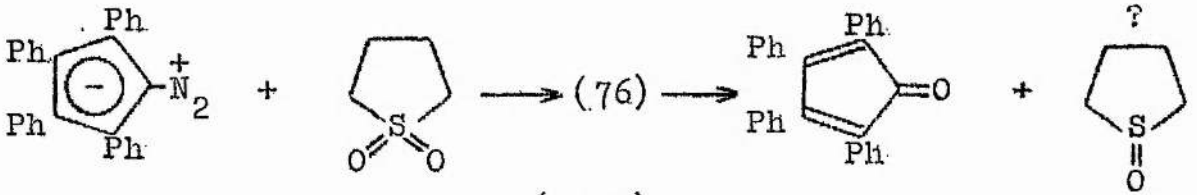


(75)



(76)

diazocyclopentadiene was decomposed in tetrahydrothiophene-1,1-dioxide under an atmosphere of nitrogen a high yield of 2,3,4,5-tetraphenylcyclopentadienone was obtained. It seems that 2,3,4,5-tetraphenylcarbenacyclopentadiene may have reacted



(2.43)

with tetrahydrothiophene-1,1-dioxide to form (76) as an intermediate which broke down, owing to the large driving force to form 2,3,4,5-tetraphenylcyclopentadienone. The other product proposed from this postulated mechanism, tetrahydrothiophene-1-oxide, could not be detected.

(ii) Reaction between Pyridinium 2,3,4,5-tetraphenylcyclopentadienylide and Triphenylphosphine

Franzen and Wittig[133] found that trimethylammoniummethylide dissociated to trimethylamine and methylene since the latter could be trapped by addition of triphenylphosphine and benzophenone, presumably via the intermediate formation of triphenylphosphoniummethylide (see Part I, Plate 11). Although pyridinium 2,3,4,5-tetraphenylcyclopentadienylide is a stable ylide the possibility of its dissociation in solution into pyridine and 2,3,4,5-tetraphenylcarbenacyclopentadiene was briefly investigated. The ylide was heated with triphenylphosphine at 210° and it was expected that if the carbene were to be formed it would couple with the phosphine to give the known phosphonium ylide (38) which would have survived the reaction conditions. This compound (38) was not detected but a black unidentified crystalline substance was isolated in good yield. Its N.M.R. spectrum showed only a complex multiplet centred at 3.1 τ and its elemental analysis figures and molecular weight suggested an empirical formula of $C_{29}H_{20}N$.

PART III

EXPERIMENTAL

1. MATERIALS AND APPARATUS

Ultra-violet and visible spectra were measured with a Unicam S.P.800 instrument.

Infra-red spectra were obtained with either a Perkin-Elmer 137 instrument or a Perkin-Elmer 257 instrument.

N.M.R. Spectra were carried out at 34° on a Perkin-Elmer R10 spectrometer operating at 60Mc/sec., at a sweep-rate of 1.6c/sec./sec. and a sweep-width of 600c./sec..

Microanalyses were carried out by Dr.'s Weiler and Strauss, Oxford, Dr.A.Bernhardt, Mullheim, Germany, and Mr.J.B.Bews, St.Andrews University, Scotland.

Column chromatography was carried out in all cases on activated alumina, Spence Type H 100/200 mesh.

Thin layer chromatography was done on silica (M.N.Kieselgel G). coated plates.

Light petroleum refers to light petroleum 40-60° unless otherwise stated.

2. PREPARATION OF SUBSTITUTED DIAZOCYCLOPENTADIENES

(i) 2,3,4,5-Tetraphenyldiazocyclopentadiene

The method of Regitz and Liedhegener[88] was used with some modification. Piperidine (5.1g., 60m.moles) and p-toluene-sulphonylazide (4.4g., 10% excess) were added to a suspension of finely ground 2,3,4,5-tetraphenylcyclopentadiene (7.4g., 20m.moles) in acetonitrile (100ml.) and the mixture was stirred and kept at 20° on a water-bath. The white suspension became deep orange in colour and after 3hr. was filtered off to give an orange solid. The solid was dissolved in a minimum amount of benzene and applied to an alumina column prepared with a 1:1 mixture of benzene and light petroleum (b.p. 80-100°). Elution with a mixture of benzene and light petroleum (b.p. 80-100°) (1:1) brought off a yellow band which gave an orange solution. Evaporation of the solvent and recrystallisation from nitromethane gave 2,3,4,5-tetraphenyldiazocyclopentadiene (5.9g., 75%) as yellow-orange needles, m.p. 148°(lit[88].149°; lit[87].143-144°).

(ii) 2,3,4-Triphenyldiazocyclopentadiene

Piperidine (5.1g., 60m.moles) and p-toluenesulphonylazide (4.4g., 10% excess) were added to a suspension of finely ground 2,3,4-triphenylcyclopentadiene (5.9g., 20m.moles) in acetonitrile (100ml.). The same procedure was followed as in the previous preparation and the dirty orange solid obtained

was dissolved in a minimum quantity of benzene and applied to an alumina column prepared with a 1:1 mixture of benzene and light petroleum (b.p. 80-100°). Elution with this mixture of solvents brought off a yellow band which gave an orange solution. The solvent was evaporated and the residue triturated with ethanol (15ml.) to give orange crystals of 2,3,4-triphenyldiazocyclopentadiene (5.1g., 80%), m.p. 158-159°(lit[88].165-167°; lit[87].159.5°). Attempts to purify the compound by recrystallisation always led to partial decomposition when the solution was heated.

(iii) 5-Bromo-2,3,4-triphenyldiazocyclopentadiene

A modification of the method described by Lloyd and Wasson[87] was used. N-Bromosuccinimide (1.2g., 7m.moles) was added to a solution of 2,3,4-triphenyldiazocyclopentadiene (2.24g., 7m.moles) in chloroform (20ml.). The solution was warmed on a water-bath at 50° for 30min. during which time it became deep red. The solution was cooled and the volume reduced to ca. 5ml. and ether (25ml.) added. The solution was washed thoroughly with water, dried (Na_2SO_4), and the solvent evaporated to give an orange residue. This was taken up in a minimum quantity of benzene and chromatographed on an alumina column prepared with benzene. The initial yellow fraction eluted with benzene gave, on evaporation of the solvent and recrystallisation from nitromethane, 5-bromo-2,3,4-triphenyl-

diazocyclopentadiene (2.5g., 90%) as yellow needles, m.p. 130-131°(lit[87].128-130°).

(iv) 5-Chloro-2,3,4-triphenyldiazocyclopentadiene

N-Chlorosuccinimide (0.5g., 3m.moles + 10% excess) was added to a solution of 2,3,4-triphenyldiazocyclopentadiene (0.96g., 3m.moles) in chloroform (20ml.). The solution was heated at 60° on a water-bath for 30min., cooled, and the solvent removed. The residue was dissolved in ether (50ml.) and the solution washed thoroughly with water, and dried (Na_2SO_4). Removal of the solvent gave an orange residue which was chromatographed on an alumina column prepared with benzene and with benzene as eluant. The initial yellow band gave an orange solution which on removal of the solvent and recrystallisation from nitromethane gave 5-chloro-2,3,4-triphenyldiazocyclopentadiene (0.85g., 84%) as goldon fluffy needles, m.p. 143-145°(decomp.). (Found: C, 71.8; H, 4.7; N, 4.1. $C_{28}H_{15}Cl$ requires C, 72.0; H, 4.5; N, 4.1).

3. REACTIONS OF 2,3,4,5-TETRAPHENYLDIAZOCYCLOPENTADIENE

(i) Pyridine

Oxygen-free nitrogen was passed through a solution of freshly distilled pyridine (5ml.) and 2,3,4,5-tetraphenyldiazocyclopentadiene (0.39g., 1m.mole) and the mixture boiled under reflux for 15min.. During this time the colour of the solution became blue-purple. The I.R. spectrum of a sample removed from the mixture showed the absence of the characteristic diazo absorption at 2000-2200cm^{-1} which confirmed completion of the reaction. The cooled mixture was poured into water (50ml.) and the dark blue gritty precipitate of pyridinium 2,3,4,5-tetraphenylcyclopentadienylide (0.42g., 95%) was filtered, washed well with water, and dried. The crude ylide which melted at 190-195°(lit^{94}.208-210°) did not depress the melting point of an authentic sample.

Hydrobromic acid (0.2ml., 47%) was added to a solution of the pyridinium ylide (0.22g., 0.5m.mole) in ethanol (10ml.) and the deep red colour changed to yellow. Charcoal (0.2g.) was added and the solution was boiled for 2min. and then filtered while still hot. Ether was added to the cooled solution until the bromide precipitated (0.15g., 58%). A sample was recrystallised from ethanol as pale yellow needles, m.p. 208-210°(lit^{94}.213-215°).

(ii) 4-Methylpyridine

A solution of 2,3,4,5-tetraphenyldiazocyclopentadiene (0.39g., 1m.mole) in freshly distilled 4-methylpyridine (5ml.) was treated under the same conditions as described in the previous experiment to give 4-methylpyridinium 2,3,4,5-tetraphenylcyclopentadienylide (0.43g., 96%). The crude ylide had m.p. 201-203°(lit[94].208-210°).

Hydrobromic acid (0.2ml., 47%) was added to a solution of the 4-methylpyridinium ylide (0.23g., 0.5m.mole) in ethanol (5ml.). Ether (10ml.) was added to the yellow solution to give a yellow solid which was recrystallised from ethanol to give N-(2,3,4,5-tetraphenylcyclopentadienyl)-4-methylpyridinium bromide (0.14g., 50%) as yellow needles, m.p. 218-220°(lit[94].218-220°).

(iii) 2-Methylpyridine

A solution of 2,3,4,5-tetraphenyldiazocyclopentadiene (0.39g., 1m.mole) in freshly distilled 2-methylpyridine (5ml.) was subjected to the same conditions as in the case of pyridine to give 2-methylpyridinium 2,3,4,5-tetraphenylcyclopentadienylide (0.40g., 86%). The crude ylide melted at 190-195°.

Hydrobromic acid (0.2ml., 47%) was added to a solution of the 2-methylpyridinium ylide (0.23g., 0.5m.mole) in ethanol. Ether (5ml.) was added to the yellow solution to give a

yellow precipitate which was recrystallised from ethanol, with ether added to initiate crystallisation, to give N-(2,3,4,5-tetraphenylcyclopentadienyl)-2-methylpyridinium bromide (0.12g., 44%) as yellow needles, m.p. 198-200°.

(iv) 2,6-Dimethylpyridine

2,3,4,5-Tetraphenyldiazocyclopentadiene (0.8g., 2m.moles) was added to dried freshly distilled 2,6-dimethylpyridine (5ml.). Oxygen-free nitrogen was passed through the mixture which was gently warmed on an oil-bath to the reflux temperature of 2,6-dimethylpyridine. A deep blue solid precipitated after the solution had boiled under reflux for 5min.; After a further 5min. the mixture was cooled and water was added to give a semi-crystalline precipitate of 2,6-dimethylpyridinium 2,3,4,5-tetraphenylcyclopentadienylide (0.88g., 90%), which was washed well with water.

Perchloric acid (0.2ml., 60%) was added to a solution of the ylide (0.48g., 1m.mole) dissolved in a minimum amount of methanol. The solution was warmed gently. A yellow solid separated on cooling and addition of ether (15ml.). The solid was filtered and washed with ether to give N-(2,3,4,5-tetraphenylcyclopentadienyl)-2,6-dimethylpyridinium perchlorate (0.35g., 62%). A sample was recrystallised from ethanol to give pale yellow needles, m.p. 277-280°. (Found: C, 74.3; H, 5.2; N, 2.5. $C_{36}H_{30}NO_4Cl$ requires C, 75.0; H, 5.2; N, 2.4).

Hydrolysis of the perchlorate. The perchlorate (0.14g., 0.25m.mole) was suspended in water (5ml.) and ethanol (2ml.). A solution of 2N sodium hydroxide (0.5ml.) was added and the mixture was left for 12hr. during which time the pale yellow suspension became dark blue. The solid was filtered and washed with dilute sodium hydroxide solution, water, and finally a little ethanol to give dark blue crystals of 2,6-dimethylpyridinium 2,3,4,5-tetraphenylcyclopentadienylide (0.065g., 60%), m.p. 206-208°. (Found: N, 3.1. $C_{36}H_{29}N$ requires N, 3.0).

(v) Triphenylamine

2,3,4,5-Tetraphenyldiazocyclopentadiene (0.78g., 2m.moles) and triphenylamine (1.5g., 6m.moles) were thoroughly mixed and oxygen-free nitrogen was passed through the reaction flask. The mixture was gently warmed on an oil-bath until the reactants became a homogeneous red liquid, and at 140° nitrogen was evolved. After 15 min. at this temperature the solution was cooled. Thin layer chromatography of a sample of the mixture in benzene showed that a number of new products had been formed. When the reaction mixture, dissolved in a 1:1 mixture of benzene and light petroleum, was applied to an alumina column no tractable material could be isolated.

(vi) Diphenylamine

2,3,4,5-Tetraphenyldiazocyclopentadiene (0.78g., 2m.moles) and diphenylamine (0.68g., 4m.moles) were thoroughly mixed and oxygen-free nitrogen was passed through the reaction flask. The mixture was heated as in the previous experiment until the evolution of nitrogen had ceased and the colour of the reaction mixture had become deep green. The mixture was cooled and dissolved in a minimum of light petroleum and benzene (1:1) and chromatographed on an alumina column prepared with light petroleum. The initial yellow band was eluted with a 25% solution of benzene in light petroleum and removal of the solvent left a bright yellow solid. This was recrystallised by dissolving it in a minimum of light petroleum at room temperature and cooling the solution to -70°. Rapid filtration gave 1-(N,N'-diphenylamino)-2,3,4,5-tetraphenylcyclopentadiene (0.55g., 52%), a bright yellow amorphous solid, m.p. 76-78°. (Found: C, 90.1; H, 6.2. $C_{41}H_{31}N$ requires C, 91.6; H, 5.8).

(vii) Triphenylphosphine

2,3,4,5-Tetraphenyldiazocyclopentadiene (2.34g., 6m.moles) and triphenylphosphine (2.62g., 10m.moles) were ground up together to a powder. The mixture was placed in a reaction flask and flushed with oxygen-free nitrogen. It was then heated under an atmosphere of nitrogen for 10 min. on an

oil-bath at 150°. Nitrogen was evolved from the mixture and the reaction then proceeded vigorously for a few minutes until the mixture solidified. Ether was added to the cooled solid and a yellow crystalline precipitate appeared which was filtered and washed with ether. The precipitate was recrystallised from a mixture of nitromethane and benzene to give bright yellow crystals of triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide (2.1g., 52%), m.p. 297-299°. (Found: C, 89.4; H, 5.8 . $C_{47}H_{35}P$ requires C, 89.5; H, 5.7%).

Perchloric acid (0.1ml., 60%) was added to a solution of triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide (0.315g., 0.5m.mole) in a minimum amount of ethanol. The yellow solution immediately became colourless and on addition of ether (10ml.) a pale, almost colourless, crystalline precipitate separated. This was filtered and washed well with ether to give triphenyl(2,3,4,5-tetraphenylcyclopentadienyl)-phosphonium perchlorate (0.35g., 97%). A sample recrystallised from methanol to give colourless plates had m.p. 255°(decomp.). (Found: C, 76.7; H, 5.2; Cl, 5.1. $C_{47}H_{36}PClO_4$ requires C, 77.15; H, 4.9; Cl, 4.85%).

(viii) Triphenylarsine

A mixture of 2,3,4,5-tetraphenyldiazocyclopentadiene (2.34g., 6m.moles) and triphenylarsine (3.06g., 10m.moles)

was treated under the same conditions as in the previous experiment. The work-up with ether gave a dirty yellow crystalline precipitate of triphenylarsonium 2,3,4,5- tetraphenylcyclopentadienylide (2.1g., 50%). A sample was recrystallised from nitromethane to give small yellow needles, m.p. 228-230°(decomp.). (Found: C, 82.7; H, 5.75. $C_{47}H_{35}As$ requires C, 83.6; H, 5.2%).

Perchloric acid (0.1ml.) was added to a solution of triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (0.34g., 0.5m.mole) in ethanol (5ml.). A pale yellow precipitate immediately appeared and precipitation was completed by the addition of ether (10ml.). The solid was filtered and recrystallised from ethanol to give pale yellow crystals of triphenyl(2,3,4,5-tetraphenylcyclopentadienyl)arsonium perchlorate (0.41g., 81%), m.p. 216-218°(decomp.). (Found: C, 72.3; H, 4.7. $C_{47}H_{36}AsClO_4$ requires C, 72.8; H, 4.65%).

(ix) Triphenylstibine

A mixture of 2,3,4,5-tetraphenyldiazocyclopentadiene (2.34g., 6m.moles) and triphenylstibine (3.53g., 10m.moles) was treated under the same conditions as in the case of triphenylphosphine. When the reaction mixture was cooled and ether (15ml.) was added lustrous crystals separated out of the solution. These were filtered and washed with ether

to give yellow-green crystals of triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (2.4g., 55%), m.p. 196-198°. Attempts to recrystallise this compound failed due to rapid hydrolysis from moisture in the solvent and in the atmosphere when in solution. A sample for analysis was prepared by following the above procedure, using dust-free conditions, and washing well with ether. (Found: C, 77.8; H, 4.9. $C_{47}H_{35}Sb$ requires C, 78.2; H, 4.9%).

Perchloric acid (0.1ml., 60%) was added to a suspension of triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (0.36g., 0.5m.mole) in ethanol (1ml.). The mixture became bright yellow and solidified. Ether (10ml.) was added and the yellow solid was filtered and washed with ether to give triphenyl(2,3,4,5-tetraphenylcyclopentadienyl)stibonium perchlorate (0.38g., 92%). A sample was recrystallised rapidly from ethanol to give bright yellow-orānge plates, m.p. 195-196°(decomp.). (Found: C, 67.7; H, 4.7; Cl, 4.7. $C_{47}H_{36}SbClO_4$ requires C, 68.8; H, 4.65; Cl, 4.4%). It should be noted that recrystallisation of the perchlorate was done rapidly to avoid hydrolysis of the salt which occurred if it was left in ethanolic solution for more than about 10 min..

(x) Triphenylbismuth

2,3,4,5-Tetraphenyldiazocyclopentadiene (2.34g., 6m.moles) and triphenylbismuth (4.4g., 10m.moles) were thoroughly mixed and heated gently on an oil-bath under an atmosphere of nitrogen. At 140° nitrogen was evolved from the reaction mixture whose colour changed from red to deep blue. After 10 min. at this temperature the mixture solidified to a blue mass and on cooling and addition of ether (15ml.) a deep blue-purple coloured solution resulted. To this was added light petroleum (10ml.) which gave a blue precipitate. This was filtered to give triphenylbismuthonium 2,3,4,5-tetraphenylcyclopentadienylide (3.4g), contaminated with triphenylbismuth as shown by thin layer chromatography. The crude blue amorphous solid melted with decomposition >165°. Attempts to chromatograph or recrystallise the solid failed owing to its decomposition in solution.

(xi) Diphenylsulphide

2,3,4,5-Tetraphenyldiazocyclopentadiene (3.96g., 10m.moles) was dissolved in diphenylsulphide (5.58g., 30m.moles) at 100°. Oxygen-free nitrogen was passed through the solution for 5 min. before the temperature was raised to 150°. The solution, still under an atmosphere of nitrogen, was kept at this temperature on an oil-bath for 10 min. until the evolution of nitrogen from the reaction had ceased. The I.R. spectrum

of a sample removed from the solution showed the absence of any absorption due to a diazo group. Ether (15ml.) was added to the cooled solution and the pale yellow crystals which separated were filtered and washed with ether to give diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (4.5g., 80%). A sample was recrystallised from a mixture of benzene and light petroleum as pale yellow prisms, m.p. 218°(decomp.), insoluble in perchloric acid. (Found: C, 88.3; H, 5.5. $C_{41}H_{30}S$ requires C,88.8; H, 5.4%).

(xii) Methylphenylsulphide

Following the procedure described in the previous experiment 2,3,4,5-tetraphenyldiazocyclopentadiene (3.96g., 10m.moles) was decomposed in methylphenylsulphide (3.72g., 30m.moles). The work-up with ether gave very pale yellow crystals of methylphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (3.2g., 65%). Recrystallised from a mixture of light petroleum and benzene it had m.p. 204-206°(decomp.). (Found: C, 87.9; H, 5.1. $C_{36}H_{28}S$ requires C, 87.8; H, 5.7%).

Perchloric acid (0.1ml., 70%) was added to a solution of methylphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (0.49g., 1m.mole) in ethanol (10ml.) to give an immediate bright yellow precipitate. Ether (10ml.) was added and the yellow salt filtered, washed with ethanol and recrystallised

from glacial acetic acid, with ether added to initiate crystallisation, to give methylphenyl(2,3,4,5-tetraphenylcyclopentadienyl)sulphonium perchlorate (0.53g., 90%), as bright yellow needles, m.p. 155°(decomp.). (Found: C, 72.8; H, 4.95. $C_{36}H_{29}SClO_4$ requires C, 73.0; H, 4.9%).

(xiii) Diphenylselenide

Following the procedure adopted in the previous two experiments 2,3,4,5-tetraphenyldiazocyclopentadiene (3.96g., 10m.moles) was decomposed in diphenylselenide (6.99g., 30m.moles). The work-up with ether produced bright yellow crystals which were filtered and washed with ether to give diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide (5.7g., 90%). This was recrystallised from cyclohexane to give bright yellow crystals, m.p. 188-190°(decomp.), insoluble in perchloric acid. (Found: C, 82.4; H, 5.1. $C_{41}H_{30}Se$ requires C, 81.9; H, 5.0%)

4. REACTION OF DIAZOCYCLOPENTADIENES WITH PHOSPHINES

(i) 2,3,4-Triphenyldiazocyclopentadiene and Triphenylphosphine

In a melt.- 2,3,4-Triphenyldiazocyclopentadiene (0.64g., 2m.moles) and triphenylphosphine (0.786g., 3m.moles) were ground up well together and heated on an oil-bath under an atmosphere of nitrogen. The solution became deep red at 120° and on further heating (180°) there was a rapid evolution of nitrogen from the reaction mixture. Thin layer chromatography indicated the formation of a number of decomposition products but none of these could be isolated using column chromatography.

The experiment was repeated but in this case the temperature of the oil-bath was not allowed to exceed 140°. After 10 min. at this temperature the solution was cooled and a mixture of ether (5ml.) and light petroleum (15ml) was added. The orange precipitate which separated was filtered and recrystallised from chloroform, with ether added to initiate crystallisation, to give 2,3,4-triphenylcyclopentadienylidene triphenylphosphazine (1.0g., 70%) as orange needles, m.p. 165°. (Found: C, 84.2; H, 5.0. $C_{41}H_{31}N_2P$ requires C, 84.5; H, 5.3%).

In a solvent.- 2,3,4-Triphenyldiazocyclopentadiene (0.64g., 2m.moles) was dissolved in light petroleum (15ml.) and benzene (5ml.). Triphenylphosphine (0.524g., 2m.moles.)

was added and the mixture was warmed at 40° for 5 min. and then left at room temperature for 2 hr.. The orange precipitate was filtered off to give 2,3,4-triphenylcyclopentadienylidene phosphazine (1.02g., 90%). A sample was recrystallised from chloroform, with ether added to initiate crystallisation, as orange needles, m.p. 165°.

Perchloric acid (0.2ml., 60%) was added to a suspension of the phosphazine (0.58g., 0.5m.mole) in acetonitrile (10ml.). The solution became clear and ether (10ml.) was added. Pale red crystals separated out of the solution and these were filtered and washed with ether to give 2,3,4-triphenylcyclopentadienylidene triphenylphosphazonium perchlorate (0.55g., 80%). A sample was recrystallised from methanol as red prisms, m.p. 222-225°(decomp.). (Found: C, 71.6; H, 4.6; N, 4.2. $C_{41}H_{32}N_2ClO_4P$ requires C, 71.8; H, 4.7; N, 4.1%).

(ii) 5-Chloro-2,3,4-triphenyldiazocyclopentadiene and Triphenylphosphine

In a melt.- A mixture of 5-chloro-2,3,4-triphenyldiazocyclopentadiene (0.355g., 1m.mole) and triphenylphosphine (0.524g., 2m.moles) was heated on an oil-bath at 130° until the solution became dark red. After 5 min. the solution was cooled and ethanol (5ml.) and perchloric acid (0.1ml., 60%) were added. Ether (15ml.) was then added to the resultant

orange solution and the red crystals which separated were filtered and washed with ether to give 5-chloro-2,3,4-triphenylcyclopentadienylidene triphenylphosphazonium perchlorate (0.39g., 55%). A sample was recrystallised from methanol, with ether added to initiate crystallisation, as granular orange prisms, m.p. 243-245°(decomp.). (Found: C, 71.8; H, 4.7; N, 4.1. $C_{41}H_{31}ClO_4P$ requires C, 72.0; H, 4.5; N, 4.1%).

In a solvent.- A solution of 5-chloro-2,3,4-triphenyldiazocyclopentadiene (0.355g., 1m.mole) and triphenylphosphine (0.262g., 1m.mole) in acetonitrile (20ml.) was boiled for 2 hr.. On evaporation of the solvent and chromatography of the residue on a column of alumina 5-chloro-2,3,4-triphenyldiazocyclopentadiene was recovered unchanged.

(iii) 5-Bromo-2,3,4-triphenyldiazocyclopentadiene and Triphenylphosphine

In a melt.- A mixture of 5-bromo-2,3,4-triphenyldiazocyclopentadiene (0.399g., 1m.mole) and triphenylphosphine (0.524g., 2m.moles) was heated on an oil-bath at 130° and the solution became dark red. After 5 min. the solution was cooled and dissolved in a small amount of benzene and chromatographed on an alumina column prepared with light petroleum. The first band (yellow) eluted with benzene and

light petroleum (1:1) gave unreacted 5-bromo-2,3,4-triphenyldiazocyclopentadiene (0.15g.). A second band (orange) was eluted with a (1:1) mixture of benzene and chloroform to give a red solution. Evaporation of the solvent gave an oily residue which could not be recrystallised. Addition of perchloric acid to an ethanolic solution of the residue did not afford an isolable salt.

In a solvent.- 5-Bromo-2,3,4-triphenyldiazocyclopentadiene (0.399g., 1m.mole) was recovered unchanged after heating it to reflux with acetonitrile (20ml.) and triphenylphosphine (0.262g., 1m.mole) for 3 hr..

(iv) 2,3,4,5-Tetraphenyldiazocyclopentadiene and Tri-n-butylphosphine

In a melt.- 2,3,4,5-Tetraphenyldiazocyclopentadiene (0.396g., 1m.mole) and tri-n-butylphosphine (0.4g., 2m.moles) were warmed together on an oil-bath under an atmosphere of nitrogen. The colour of the solution became deep red (100°) characteristic of the formation of a phosphazine. When the temperature was raised to 170° there was a rapid evolution of nitrogen as a vigorous reaction ensued. No identifiable substances were isolated from the decomposition reaction.

In a solvent.- Tri-n-butylphosphine (0.202g., 1m.mole) was added to a solution of 2,3,4,5-tetraphenyldiazocyclopentadiene(0.396g., 1m.mole) in light petroleum (15ml.) and

and ether (5ml.) and the mixture was left for 3 hr. at room temperature. The orange precipitate which formed was collected and recrystallisation from nitromethane gave 2,3,4,5-tetraphenylcyclopentadienone hydrazone (0.24g., 60%) as scarlet needles, m.p. 240-242°(decomp.). (Found: C, 87.1; H, 5.6; N, 7.35. $C_{29}H_{22}N_2$ requires C, 87.3; H, 5.5; N, 7.0%). (Although dry solvents were used no precautions were taken against the ready hydrolysis of the intermediate phosphazine by moisture from the atmosphere).

In the presence of p-nitrobenzaldehyde.- A solution of 2,3,4,5-tetraphenyldiazocyclopentadiene (0.396g., 1m.mole), tri-n-butylphosphine (0.202g., 1m.mole), and p-nitrobenzaldehyde (0.151g., 1m.mole) in dry redistilled benzene (15ml.) was heated to reflux for 4 hr., during which time the colour of the solution darkened. The solution, after the volume had been reduced (ca.5ml.), was applied to an alumina column prepared with light petroleum and benzene (1:1). The first yellow band eluted with a (1:1) mixture of light petroleum and benzene gave unreacted diazo compound (0.06g.). The second band (brown-red) eluted with benzene gave, on evaporation of the solvent and trituration with nitromethane, p-nitrobenzaldehyde 2,3,4,5-tetraphenylcyclopentadienone hydrazone (0.30g., 55%). A sample was recrystallised from nitromethane as deep maroon needles, m.p. 245-246°. (Found:

C, 81.3; H, 4.7; N, 8.0. $C_{36}H_{25}N_3O_2$ requires C, 81.4; H, 4.7; N, 7.9%). A third band (red), eluted with chloroform gave 2,3,4,5-tetraphenylcyclopentadienone hydrazone (0.12g.).

Preparation of p-nitrobenzaldehyde 2,3,4,5-tetraphenylcyclopentadienone hydrazone.- A solution of 2,3,4,5-tetraphenylcyclopentadienone hydrazone (0.28g., 1m.mole) and p-nitrobenzaldehyde (0.151g., 1m.mole) in chloroform was heated to reflux for 3 hr.. The solvent was removed to leave a red residue which gave a dark precipitate when triturated with warm benzene (5ml.). The precipitation was completed by addition of methanol (5ml.) and the solid was filtered and washed with a little cold methanol. The solid was recrystallised from nitromethane to give p-nitrobenzaldehyde 2,3,4,5-tetraphenylcyclopentadienone hydrazone (0.37g., 85%), m.p. 246°.

Oxidation of 2,3,4,5-tetraphenylcyclopentadienone hydrazone.- 2,3,4,5-Tetraphenylcyclopentadienone hydrazone (0.28g., 1m.mole), yellow mercuric oxide (0.3g.), and anhydrous sodium sulphate (0.1g.) were ground up well together and placed in a stoppered tube. Dry ether (10ml.) was added followed by a concentrated solution of alcaholic potassium hydroxide (0.1ml.) and the mixture was shaken well for 5 min.. The ethereal solution (orange) was filtered and the residue washed with ether. The solvent was removed from the combined

solution and washings to give an orange residue which on trituration with ethanol gave 2,3,4,5-tetraphenyldiazocyclopentadiene (0.25g., 90%), m.p. 148°(decomp.).

(v) 2,3,4,5-Tetrachlorodiazocyclopentadiene and Triphenylphosphine

In a melt.- 2,3,4,5-Tetrachlorodiazocyclopentadiene (0.85g., 5m.moles) and triphenylphosphine (2.1g., 8m.moles) were ground up well together and heated gently at 90° on a water-bath. At this temperature the colour of the mixture changed from red to deep scarlet. (Above this temperature a violent reaction ensued with the evolution of nitrogen, resulting in the formation of a black tar). After 5 min. the mixture was cooled and dissolved in a minimum amount of benzene and applied to an alumina column prepared with light petroleum. The first colourless band eluted with a mixture of equal volumes of benzene and light petroleum gave unreacted triphenylphosphine. The second band (red) eluted with benzene gave a red solid which was recrystallised from cyclohexane to give 2,3,4,5-tetrachlorocyclopentadienylidene triphenylphosphazine as red prisms, m.p. 130-132°(decomp.) (lit[89].132°). (Found: C, 56.3; H, 3.2; N, 5.8; Cl, 28.4. $C_{23}H_{15}N_2Cl_4P$ requires C, 57.0; H, 3.1; N, 5.7; Cl, 28.9%).

In a solvent.- 2,3,4,5-Tetrachlorodiazocyclopentadiene (0.85g., 5m.moles) was dissolved in light petroleum (15ml.)

and to this was added triphenylphosphine (1.31g., 5m.moles). The solution was left for 3 hr. at room temperature and then the dark red precipitate which separated was filtered to give 2,3,4,5-tetrachlorocyclopentadienylidene triphenylphosphazine (1.96g., 91%), and was recrystallised from cyclohexane as red needles, m.p. 131°(decomp.).

The phosphazine (0.432g., 1m.mole) was kept exposed to the atmosphere for 24 hr. during which time it lost its crystalline appearance and became sticky. The solid was recrystallised from a mixture of petroleum and methylene chloride to give 2,3,4,5-tetrachlorocyclopentadienone hydrazone (0.11g., 65%) as scarlet needles, m.p. 174-176° (lit[89].176°). (Found: C, 26.7; H, 1.7; N, 12.1; Cl, 59.0. $C_5H_2N_2Cl_4$ requires C, 25.9; H, 0.9; N, 12.1; Cl, 61.2%). The solvent was removed from the mother-liquor of the recrystallisation to leave a red coloured residue. This was boiled up with water which was decanted from the insoluble material and colourless crystals separated out of the aqueous solution. These were filtered and dried to give triphenylphosphine oxide (0.12g., 45%) as colourless plates, m.p. 150°.

Decomposition of 2,3,4,5-tetrachlorocyclopentadienylidene triphenylphosphazine.- Heating the phosphazine above 130° at atmospheric pressure resulted in a vigorous evolution of nitrogen and no tractable material could be isolated from the tarry decomposition products.

The phosphazine (0.432g., 1m.mole) was placed in a glass tube and heated to 110° under vacuum (0.05mm.). Under these conditions the compound evolved nitrogen gently and became a black mass. Initially a small red band sublimed up the tube and after 30 min. a larger yellow-orange band appeared which was followed by a small amount of a white substance. The red band (0.02g.), m.p. 128°(decomp.) was undecomposed phosphazine. The yellow band (0.06g, 35%) m.p. 106-108°(decomp.) was 2,3,4,5-tetrachlorodiazocyclopentadiene and the white substance (0.018g.), m.p. 148° appeared to be triphenylphosphine oxide.

5. OTHER REACTIONS OF DIAZOCYCLOPENTADIENES

(i) 2,3,4,5-Tetrachlorodiazocyclopentadiene and Copper Powder

Copper powder (0.4g.) was added to a solution of 2,3,4,5-tetrachlorodiazocyclopentadiene (0.864g., 2m.moles) in ethanol (30ml.) and the mixture was heated to reflux for 2 hr.. The dark coloured solution was filtered and the solvent removed from the filtrate to give a dark red-brown residue. This was recrystallised from a mixture of benzene and nitromethane to give 2,3,4,5-tetrachlorocyclopentadienone azine (0.54g., 65%) as maroon needles, m.p. 180°. (Found: C, 28.2; H, 0.0; N, 7.4; Cl, 64.0. $C_{10}N_2Cl_8$ requires C, 27.8; H, 0.0; N, 6.5; Cl, 65.7%).

(ii) Attempted reaction of 2,3,4,5-Tetraphenyldiazocyclopentadiene with Dichlorocarbene

Chloroform (0.3ml.) was added dropwise to a stirred mixture of potassium t-butoxide (0.3g.) and 2,3,4,5-tetraphenyldiazocyclopentadiene (0.32g., 1m.mole) in dry benzene (10ml.). Stirring was continued for 18 hr. with the addition of more potassium t-butoxide (0.3g.) after 6 hr.. The solution was quenched with water (50ml.) and extracted with benzene. The benzene extract was washed well with water, dried (Na_2SO_4), and evaporated to give unchanged diazo compound in quantitative yield.

(iii) 2,3,4,5-Tetraphenyldiazocyclopentadiene and Nitrosobenzene

A mixture of 2,3,4,5-tetraphenyldiazocyclopentadiene (0.79g., 2m.moles) and nitrosobenzene (0.214g., 2m.moles) in chloroform (20ml.) was heated to reflux for 18 hr. during which time (after 6 hr.) a further quantity of nitrosobenzene (0.107g., 1m.mole) was added. Chromatography of the residue in benzene on an alumina column prepared with light petroleum gave first of all a yellow band, eluted with a (1:1) mixture of light petroleum and benzene. This gave unchanged diazo compound (0.31g.). Benzene eluted a trace of 2,3,4,5-tetraphenylcyclopentadienone followed by a small amount of unreacted nitrosobenzene. Elution with chloroform gave a

green band which on removal of the solvent and addition of ethanol (10ml.) gave a khaki-green precipitate of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.19g., 22%). A sample was recrystallised from n-propanol as khaki-green needles, m.p. 224-226°. (Found: C, 88.2; H, 5.1; N, 2.9. $C_{35}H_{25}NO$ requires C, 88.4; H, 5.25; N, 2.9%).

(iv) 2,3,4-Triphenyldiazocyclopentadiene and Nitrosobenzene

A solution of 2,3,4-triphenyldiazocyclopentadiene (0.64g., 2m.moles) and nitrosobenzene (0.214g., 2m.moles) in chloroform (20ml.) was subjected to the same conditions as in the previous experiment. The chromatography products were unchanged diazo compound (0.2g.), an unidentified red oil and a green solid. This solid was recrystallised from ethanol to give N-phenyl 2,3,4-triphenylcyclopentadienone ketoxime (0.096g., 12%) as green needles, m.p. 156-158°. (Found: C, 87.2; H, 5.1; N, 3.5. $C_{29}H_{21}NO$ requires C, 87.1; H, 5.25; N, 3.5%).

6. REACTIONS OF 2,3,4,5-TETRAPHENYLCYCLOPENTADIENYLIDES

(i) Triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide

a) Attempted Hydrolysis.- Sodium hydroxide (1g.) was dissolved in ethanol (25ml.). Triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (0.34g., 0.5m.mole) was added to this solution as a suspension and the mixture heated to reflux for 18 hr.. The solutin was quenched with water (50ml.) and extracted with chloroform. The chloroform extract was washed with water, dried (Na_2SO_4), and on removal of the solvent an oily residue remained. Addition of ether gave the unchanged ylide in quantitative yield.

b) Benzaldehyde.- Triphenylarsonium 2,3,4,5-tetraphenyl-cyclopentadienylide (0.67g. 1m.mole) and freshly redistilled benzaldehyde (0.106g., 1m.mole) were dissolved in carbon tetrachloride (25ml.) and the solution boiled for 5 hr.. A further quantity of redistilled benzaldehyde (0.053g., 0.5m.mole) was added and the boiling continued for another 13 hr.. The solvent was removed and ether (10ml.) was added to the red residue whereupon a pale yellow precipitate appeared. This was filtered and washed with ether to give unreacted arsonium ylide (0.3g.). The mother-liquor, on removal of the solvent, was dissolved in a small amount of benzene and applied to an alumina column prepared with light petroleum and benzene. The initial band (orange) eluted

with this mixture of solvents gave a red solution. Evaporation of the solvents and recrystallisation of the residue from glacial acetic acid gave 1,2,3,4,6-pentaphenylfulvene (0.073g., 16%) as deep red-brown prisms, m.p. 197-199°(lit[134].200-201°). A second band (purple) eluted with benzene gave, after evaporation of the solvent and trituration with ethanol, sparkling black crystals of 2,3,4,5-tetraphenylcyclopentadienone (0.004g., 1.3%), m.p. 214-216° . A pale yellow band remained at the top of the column and this was eluted with methanol. The solvent was removed and water added to the yellow residue. The water was boiled for 5 min. and left to cool. White crystals separated and after they had been filtered and dried gave triphenylarsine oxide (0.026g., 8%), m.p. 192°.

The reaction was repeated using chloroform as the solvent and a similar yield (17%) of 1,2,3,4,6-pentaphenylfulvene was obtained.

c) p-Nitrobenzaldehyde.- Triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (0.67g., 1m.mole) and p-nitrobenzaldehyde (0.15g., 1m.mole) were dissolved in carbon tetrachloride (25ml.) and the mixture was heated to reflux for 4 hr.. During this time the solution became deep red. The solvent was removed and the red residue taken up in a minimum amount of benzene and applied to an alumina column

prepared with a (1:1) mixture of benzene and light petroleum. A single brown band was eluted with benzene to give, after removal of the solvent and trituration with nitromethane, 6-p-nitrophenyl-1,2,3,4-tetraphenylfulvene (0.48g., 95%). A sample was recrystallised from nitromethane as red-brown needles, m.p. 232-234°. (Found: C, 84.0; H, 4.8; N, 3.5. $C_{36}H_{25}NO_2$ requires C, 84.0; H, 5.6; N, 3.2%). The pale yellow band remaining at the top of the column was eluted with methanol and the work-up of the yellow solution, identical to that described in the previous experiment, gave triphenylarsine oxide (0.12g., 41%).

d) Nitrosobenzene.- A mixture of triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (0.67g., 1m.mole) and nitrosobenzene (0.107g., 1m.mole) in benzene (25ml.) was heated to reflux for 6 hr.. (After the initial 3 hr. a further quantity of nitrosobenzene (0.054g., 0.5m.mole) was added). The solvent was reduced in volume (ca.5ml.) and the solution was applied to an alumina column prepared with a (2:1) mixture of light petroleum and benzene. This mixture of solvents eluted a red band which gave a red solution but which was shown by thin layer chromatography to contain a colourless compound. On changing the solvent to a (1:5) mixture of light petroleum and benzene a small purple band was eluted which gave a trace of 2,3,4,5-tetraphenylcyclopentadienone.

Benzene eluted a green band which gave a red-green solution. The solvent was evaporated and the residue was treated with a little ethanol (5ml.) to give N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.23g., 48%). This was identical to the compound prepared from the reaction of 2,3,4,5-tetraphenyldiazocyclopentadiene with nitrosobenzene (Experiment 5, iii). The final band on the column was yellow and this was eluted with chloroform to give an off-white solid after the solvent had been removed. Recrystallisation of the solid from water afforded colourless plates of triphenylarsine oxide (0.032g., 10%).

The red solution which was initially eluted from the column was treated as follows. Alumina (5g.) was added to the solution and the solvent was removed to give a mixture of the residue with dry alumina. This was applied to a fresh column of alumina prepared with light petroleum. A (10:1) mixture of light petroleum and benzene eluted a colourless band which after evaporation of the solvent and recrystallisation of the colourless residue from ethanol gave triphenylarsine (0.10g., 33%) as colourless needles. When the ratio of light petroleum to benzene was changed to (1:2) a red band was eluted which gave a bright red solution. The solvent was removed and the residue recrystallised from nitromethane to give 2,3,4,5-tetraphenylcyclopentadienone

anil (0.16g., 35%) as crimson prisms, m.p. 232-235°. (Found: C, 90.8; H, 5.9; N, 3.2. $C_{35}H_{25}N$ requires C, 91.6; H, 5.6; N, 3.1%).

e) Attempted reaction with Dichlorocarbene.- Potassium t-butoxide (0.3g.) was added to a solution of triphenylarsonium 2,3,4,5-tetraphenylcyclopentadienylide (0.335g., 0.5m.mole) in benzene (20ml.) and the mixture was stirred at room temperature while chloroform (0.3ml.) was added. Stirring was continued for 48 hr. and the yellow solution became pale red. The solution was filtered and the benzene solution washed thoroughly with water and dried (Na_2SO_4). Removal of the solvent and addition of ether (15ml.) gave a pale yellow precipitate which was filtered to give unchanged arsonium ylide (0.25g.). The ether was evaporated from the filtrate and the red residue was dissolved in a minimum of benzene and applied to an alumina column prepared with light petroleum. A (4:1) mixture of light petroleum and benzene eluted a pale yellow band which gave triphenylarsine (0.01g.). Benzene eluted a purple band of 2,3,4,5-tetraphenylcyclopentadienone (0.018g.).

(ii) Triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide

The ylide did not react with those reagents mentioned in Experiment 6,i) under the conditions described and was recovered unchanged.

(iii) Triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide

a) Hydrolysis- Triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (0.36g., 0.5m.mole) was added to ethanol (15ml.) and the mixture heated to reflux for 5 min.. After the solution had cooled colourless crystals separated. These were filtered and washed with cold ethanol to give 2,3,4,5-tetraphenylcyclopentadienone (0.156g., 85%). The solvent was removed from the mother-liquor, water was added to the residue, and the mixture boiled for 3 min.. The aqueous solution was decanted while it was hot and left to cool. The colourless crystals which precipitated were filtered to give triphenylstibine oxide (0.074g., 40%).

b) Benzaldehyde.- Triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (0.72g., 1m.mole) and freshly distilled benzaldehyde (0.106g., 1m.mole) were dissolved in carbon tetrachloride (25ml.) and the mixture refluxed for 18 hr.. The solvent was removed from the deep red solution and the residue, in a little benzene, was applied to an alumina column prepared with light petroleum. Elution with a mixture of light petroleum and benzene (4:1) resulted initially in a red band, which gave a red solution, and this was followed by a pale yellow band which gave a yellow solution. The first of these solutions (red), after removal of the solvent and recrystallisation from glacial acetic acid, gave

1,2,3,4,6-pentaphenylfulvene (0.184g., 40%). The second solution (yellow) gave, after the solvent had been removed and the residue triturated with ethanol, 2,3,4,5-tetraphenylcyclopentadiene (0.055g., 15%). A final band (yellow) was brought off the column by elution with methanol, and evaporation of the solvent gave a yellow residue. This was recrystallised from water to give triphenylstibine oxide (0.092g., 25%).

c) p-Nitrobenzaldehyde.- A mixture of triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (0.721g., 1m.mole) and p-nitrobenzaldehyde (0.151g., 1m.mole) in carbon tetrachloride (25ml.) was heated to reflux for 4 hr. and it became dark red. The solvent was removed and the residue, dissolved in a little benzene, was applied to an alumina column prepared with light petroleum. Elution with benzene brought off a brown band which gave, after the solvent had been removed, red crystals of 6-p-nitrophenyl-1,2,3,4-tetraphenylfulvene (0.49g., 99%). Methanol eluted a yellow band which after the work-up gave triphenylstibine oxide (0.184g., 50%).

d) Nitrosobenzene.- Nitrosobenzene (0.053g., 0.5m.mole) was added to a solution of triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (0.36g., 0.5m.mole) in benzene (15ml.) and the mixture was refluxed for 10 min.. The solvent

was removed and the residue chromatographed on an alumina column prepared with light petroleum to give three bands. The first band (colourless) was eluted with a (1:1) mixture of light petroleum and benzene to give triphenylstibine(0.12g., 70%). After elution with benzene (to give a trace of 2,3,4,5-tetraphenylcyclopentadienone) the solvent was changed to chloroform, and this brought off a green band. The solvent was evaporated and the residue recrystallised from n-propanol to give N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.19g., 81%) identical to the compound prepared in the analogous reaction with the arsonium ylide (Experiment 6,i,d).

e) Attempted reaction with Dichlorocarbene.- Potassium t-butoxide (0.3g.) was added to a solution of triphenylstibonium 2,3,4,5-tetraphenylcyclopentadienylide (0.36g., 0.5m.mole) in benzene (20ml.). Chloroform was added dropwise and the mixture was stirred at room temperature for 48 hr.. Work-up of the solution gave 2,3,4,5-tetraphenylcyclopentadiene, 2,3,4,5-tetraphenylcyclopentadienone and other decomposition products. No 6,6-dichloro-2,3,4,5-tetraphenylfulvene was isolated.

(iv) Triphenylbismuthonium 2,3,4,5-tetraphenylcyclopentadienylide

The crude ylide was reacted with the same reactants as described in Experiment 6,i) and under the same conditions. In each case none of the many decomposition products was tractable.

(v) Diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide

a) Attempted hydrolysis.- A solution of 2N sodium hydroxide (2ml.) was added to a suspension of diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (0.55g., 1m.mole) in ethanol (20ml.) and the mixture was heated to reflux for 20 hr.. The solvent was removed and a mixture of ether (15ml.) and ethanol (5ml.) was added to the residue. The pale yellow precipitate which appeared was filtered and washed with ether to give unchanged diphenylsulphonium ylide in quantitative amount.

b) Attempted reaction with aldehydes.- An attempt was made to effect a reaction between diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide and each of the aldehydes, benzaldehyde, p-nitrobenzaldehyde, and 2,6-dinitrobenzaldehyde. The general procedure was to mix the aldehyde (1m.mole) and the ylide (1m.mole) in carbon tetrachloride (20ml.) and reflux the solution for 20 hr.. In each case a quantitative recovery of the starting materials was obtained.

c) Nitrosobenzene.- A mixture of nitrosobenzene (0.106g., 1m.mole) and diphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (0.55g., 1m.mole) in benzene (20ml.) was refluxed for 18 hr. during which time there was very little colour change. (After 3 hr. refluxing more nitrosobenzene (0.05g., 0.5m.mole) was added). The solvent was removed and ether (10ml.)

was added to give a precipitate of unchanged ylide (0.37g.) which was filtered off. The residue from the ethereal solution was applied to an alumina column prepared with benzene. Chloroform eluted a small green band which gave, after evaporation of the solvent and recrystallisation from n-propanol, N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.024g., 5%) identical to the compound isolated in the analogous reaction with the stibonium ylide (Experiment 6,iii,d)

(vi) Methylphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide

a) Hydrolysis.- A solution of 2N sodium hydroxide (2ml.) was added to a suspension of methylphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (0.49g., 1m.mole) in ethanol (20ml.) and refluxed for 10 hr.. Thin layer chromatography showed the absence of any of the ylide and the presence of a number of decomposition products including methylphenylsulphide. Column chromatography of the residue gave no tractable products.

b) Attempted reaction with Aldehydes.- Methylphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide was recovered unchanged when attempts were made to react it with either benzaldehyde, p-nitrobenzaldehyde, or 2,6-dinitrobenzaldehyde under conditions identical to those described for the analogous reactions of the diphenylsulphonium ylide.

c) Nitrosobenzene.- Methylphenylsulphonium 2,3,4,5-tetraphenylcyclopentadienylide (0.49g., 1m.mole) was dissolved in benzene (20ml.) and nitrosobenzene (0.106g., 1m.mole) was added. The mixture was heated to reflux for 3 hr. and then a further amount of nitrosobenzene (0.05g., 0.5m.mole) was added to the solution and refluxing was continued for another 12 hr.. The solvent was removed and the residue was boiled with ethanol (15ml.) for two minutes. Filtration of the hot mixture gave a small amount of unreacted sulphonium ylide (0.05g.) and the cooled ethanolic solution gave green-brown crystals of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.385g., 81%).

(vii) Diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide

a) Attempted hydrolysis.- A solution of 2N sodium hydroxide (2ml.) was added to a suspension of diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide (0.30g., 0.5m.mole) in ethanol (15ml.) and the mixture was heated to reflux for 20 hr.. A quantitative recovery of the selenonium ylide was obtained after using a work-up procedure identical to that described for the attempted hydrolysis of the diphenylsulphonium ylide (Experiment 6,v,a).

b)Attempted reaction with Aldehydes.- No reaction took place between diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide and either benzaldehyde, p-nitrobenzaldehyde, or 2,6-dinitrobenzaldehyde when the same conditions as described for the attempted reaction of the diphenylsulphonium analogue (Experiment 6,v,b) were used. A quantitative recovery of the starting materials was obtained in each case.

c) Nitrosobenzene.- A mixture of nitrosobenzene (0.106g., 1m.mole) and diphenylselenonium 2,3,4,5-tetraphenylcyclopentadienylide (0.601g., 1m.mole) in benzene (25ml.) was refluxed for 18 hr.. (A further amount of nitrosobenzene (0.053g., 0.5m.mole) was added after the first 3 hr.). After the solvent had been removed the residue, in benzene, was applied to an alumina column prepared with benzene. Chloroform eluted a green band which gave a green-red solution. The solvent was evaporated and the green residue was recrystallised from n-propanol to give N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.38g., 80%).

7. PREPARATION OF FULVENES AND N-PHENYL CYCLOPENTADIENONE ANILS

The general procedure for the preparation of fulvenes (after Lowenhein and Ulich)[134] was as follows.- A mixture of diene (2m.moles) and aldehyde (2.5m.moles) in a methanolic solution of sodium hydroxide (2g. in 50ml.) was heated to reflux for 6 hr.. In each case the suspension became darkly coloured. The work-up for each experiment is described individually.

(i) 1,2,3,4,6-Pentaphenylfulvene

The deep red crystals were filtered while the solution was still hot and recrystallised from glacial acetic acid to give 1,2,3,4,6-pentaphenylfulvene (0.64g., 70%) as deep scarlet prisms, m.p. 198-199°(lit[134].199°).

Oxidation of 1,2,3,4,6-pentaphenylfulvene.- Potassium hydroxide (0.1g.) was added to a mixture of 1,2,3,4,6-pentaphenylfulvene (0.46g., 1m.mole) and hydrogen peroxide (5ml., 30%) in dioxan (20ml.) and the solution was boiled for 3 hr.. The red solution became pale yellow and a precipitate appeared. This was filtered from the cooled solution to give benzal-2,3,4,5-tetraphenylcyclopentadiene oxide (0.28g., 60%). A sample was recrystallised from a mixture of nitromethane and benzene as white fluffy needles, m.p. 210°(red melt). (Found: C, 89.4; H, 5.3. $C_{36}H_{26}O$ requires C, 91.1; H, 5.5%).

(ii) 1,2,3,6-Tetraphenylfulvene

The brown precipitate was filtered from the hot solution, dissolved in a minimum of benzene and applied to an alumina column prepared with light petroleum. The first band (red) eluted with a (1:1) mixture of light petroleum and benzene gave, on evaporation of the solvent and recrystallisation from nitromethane, 1,2,3,6-tetraphenylfulvene (0.15g., 20%) as red-brown needles, m.p. 170°. This compound was identical to the fulvene prepared in Experiment 11,ii,b).

(iii) 6-p-Nitrophenyl-1,2,3,4-tetraphenylfulvene

The brown precipitate was filtered from the hot solution. Recrystallisation from nitromethane afforded 6-p-nitrophenyl-1,2,3,4-tetraphenylfulvene (0.6g., 60%) as red-brown needles, m.p. 232-234°, identical to the fulvene prepared in Experiment 6,i,c).

(iv) 6-p-Nitrophenyl-1,2,3-triphenylfulvene

The brown precipitate, which was filtered from the hot solution, was chromatogaphed on an alumina column prepared with light petroleum. A brown band was eluted with a (1:1) mixture of light petroleum and benzene. This fraction gave, after recrystallisation from nitromethane, 6-p-nitrophenyl-1,2,3-triphenylfulvene (0.13g., 15%) as brown needles, m.p. 163-165°. This fulvene was identical to that prepared in Experiment 11,ii,c).

(v) N-Phenyl 2,3,4,5-tetraphenylcyclopentadienone anil

a) From 2,3,4,5-tetraphenylcyclopentadiene.- Sodium ethoxide (1ml., 0.5g. sodium in 10ml. ethanol) was added to a solution of 2,3,4,5-tetraphenylcyclopentadiene (0.74g., 2m.moles) and nitrosobenzene (0.214g., 2m.moles) in benzene (20ml.) and the mixture was heated to reflux for 10 min.. The deep red solution was cooled and light petroleum was added. After the solution had stood at room temperature for 8 hr. red crystals separated. These were filtered and recrystallised from nitromethane to give N-phenyl 2,3,4,5-tetraphenylcyclopentadienone(.35g., 38%) as deep red prisms, m.p. 235°, identical to the compound obtained in Experiment 6,i,d).

b) From N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime.- Phosphorus trichloride (1ml.) was added to a solution of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.237g., 0.5m.mole) in chloroform (10ml.) and cooled in an ice-bath. The cooled mixture was stirred and slowly brought to room temperature over 5 hr.. At this stage there was no indication that any reduction to the anil had occurred. Water (2ml.) was added to the stirred solution and the mixture was left for 8 hr.. The mixture was quenched with water (25ml.) and extracted with chloroform to give 2,3,4,5-tetraphenylcyclopentadienone (0.49g., 70%), m.p. 216°.

A mixture of triphenylphosphine (0.262g., 1m.mole) and N-phenyl 2,3,4,5-tetraphenylcyclopentadienone ketoxime (0.237g., 0.5m.mole) in benzene (20ml.) was heated to reflux for 4 hr.. The solvent was evaporated from the deep red solution and the residue was chromatographed on an alumina column. The initial colourless band which was eluted with a (1:1) mixture of light petroleum and benzene gave unreacted triphenylphosphine (0.11g.). Benzene eluted a red band which gave N-phenyl 2,3,4,5-tetraphenylcyclopentadienone anil (0.184g., 80%) as deep red needles, identical to the compound prepared from 2,3,4,5-tetraphenylcyclopentadiene.

c) Attempted oxidation of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone anil.- An ethereal solution of perphthalic acid (4ml., 0.4m.mole) was added to a solution of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone anil (0.23g., 0.5m.mole) in methylene chloride (12ml.) and the stirred mixture was cooled in an ice-bath. The ice was allowed to melt and the mixture left for 8 hr.. After this period no ketoxime was detected amongst the decomposition products

A solution of hydrogen peroxide (4.5ml., ca. 1m.mole) was added to a solution of N-phenyl 2,3,4,5-tetraphenylcyclopentadienone anil (0.23g., 0.5m.mole) in glacial acetic acid (15ml.) and the mixture warmed at 70° for 3 hr.. More hydrogen peroxide was added and after 6 hr. there was no indication of the formation of the ketoxime.

(vi) N-Phenyl 2,3,4-triphenylcyclopentadienone anil

a) From 2,3,4-triphenylcyclopentadiene.- The same procedure was used as described for the preparation of the tetraphenyl analogue (Experiment 7,v ,a). N-phenyl 2,3,4-triphenylcyclopentadienone anil (0.23g., 30%) was recrystallised from nitromethane as bright scarlet needles, m.p. 190-192°. (Found: C, 90.2; H, 5.4; N, 4.2. $C_{29}H_{21}N$ requires C, 90.8; H, 5.5; N, 3.7%).

b) From N-phenyl 2,3,4-triphenylcyclopentadienone ketoxime.- A mixture of triphenylphosphine (0.262g., 1m.mole) and N-phenyl 2,3,4-triphenylcyclopentadienone ketoxime (0.236g., 0.5m.mole) in benzene (20ml.) was heated to reflux for 4 hr.. A work-up procedure similar to that described in Experiment 7,v,b) gave N-phenyl 2,3,4-triphenylcyclopentadienone anil (0.16g., 70%) as scarlet needles, and triphenylphosphine oxide (0.039g., 30%).

8. PREPARATION OF 5-BROMO-2,3,4-TRIPHENYLCYCLOPENTADIENE

N-Bromosuccinimide (1.78g., 10m.moles) was added to a solution of 2,3,4-triphenylcyclopentadiene (3.09g., 10m.mbles + 5% excess) in carbon tetrachloride (40ml.) and heated to reflux for 90 min.. The succinimide was filtered from the cooled solution and the carbon tetrachloride was removed from the filtrate to leave a green-yellow crystalline residue.

This was dissolved in a mixture of equal portions of hot methanol and chloroform and the solution boiled with active charcoal (0.5g.) for 5 min.. After the solution had been filtered and cooled a crystalline precipitate appeared. This was recrystallised from a mixture of equal volumes of chloroform and methanol to give 5-bromo-2,3,4-triphenylcyclopentadiene (2.5g., 68%) as yellow-green plates, m.p. 150-152° (lit.[135] 147°). (Found: C, 74.3; H, 4.5. $C_{23}H_{17}Br$ requires C, 74.0; H, 4.6%).

9. PREPARATION OF CYCLOPENTADIENYLIDES VIA THE 'SALT' METHOD

(i) Pyridinium 2,3,4-triphenylcyclopentadienylide

5-Bromo-2,3,4-triphenylcyclopentadiene (1.49g., 4m.moles) was dissolved in warm nitromethane (35ml.). Dry pyridine (0.316g., 4m.moles) was added and the mixture was warmed at 90° on a water-bath for 2 hr.. (A further portion of pyridine (0.16g., 2m.moles) was added after the first hour). The solvent was removed and the residue dissolved in ethanol (5ml.) and perchloric acid (0.5ml., 20% excess) was added. The orange precipitate which separated became an oil on addition of ether (15ml.) but after 2 hr. orange crystals deposited from the solution. These were filtered (1.05g., 72%) and recrystallised from ethanol to give N-(2,3,4-triphenylcyclopentadienyl)pyridinium perchlorate as yellow-orange

needles, m.p. 215-216°. (Found: C, 71.0; H, 4.9. $C_{28}H_{22}NClO_4$ requires C, 71.4; H, 4.7%).

Hydrolysis of the salt.- A suspension of the perchlorate (0.472g., 1m.mole) in aqueous ethanol (10ml., 50%) was treated with a solution of 2N sodium hydroxide (2ml.) and the mixture was stirred for 12 hr.. The purple precipitate was filtered to give pyridinium 2,3,4-triphenylcyclopentadienylide (0.32g., 85%). This compound could not be recrystallised from any of the usual solvents. The ylide had m.p. 183-186°. (Found: C, 90.4; H, 5.7; N, 3.6. $C_{28}H_{21}N$ requires C, 90.6; H, 5.7; N, 3.8%).

(ii) Triphenylphosphonium 2,3,4,5-tetraphenylcyclopentadienylide

a) A preliminary attempt to prepare the ylide was made as follows.- Triphenylphosphine (0.262g., 1m.mole) was added to a solution of 5-bromo-1,2,3,4-tetraphenylcyclopentadiene (0.45g., 1m.mole) in nitromethane (15ml.) and the mixture was warmed at 60° for 5 min.. The solution was cooled and colourless crystals separated which were filtered and recrystallised from acetonitrile to give 2,3,4,5-tetraphenylcyclopentadiene (0.28g., 75%), m.p. 176°.

b) A mixture of 5-bromo-1,2,3,4-tetraphenylcyclopentadiene (0.45g., 1m.mole) and triphenylphosphine (0.786g., 3m.moles) was heated on an oil-bath at 150° for 10 min.. The solution solidified on cooling and ether (15ml.) was added to

give a yellow precipitate of triphenyl(2,3,4,5-tetraphenyl-cyclopentadienyl)phosphonium bromide (0.68g., 96%). A solution of the salt in ethanol (8ml.) was treated with perchloric acid (0.2ml., 70%). Ether (15ml.) was added to the yellow solution and the colourless crystals were filtered, washed with ether, and recrystallised from methanol to give triphenyl(2,3,4,5-tetraphenylcyclopentadienyl)phosphonium perchlorate (0.66g., 90%), identical to the compound prepared in Experiment 3,vii).

Hydrolysis of the salt.- A solution of 2N sodium hydroxide (2ml.) was added to a suspension of triphenyl(2,3,4,5-tetraphenylcyclopentadienyl)phosphonium perchlorate (0.365g., 0.5m.mole) in ethanol (15ml.). The mixture was shaken vigorously for 10 min. and then left for 3 hr.. The pale yellow precipitate (0.29g., 93%) was filtered and recrystallised from a mixture of benzene and nitromethane to give triphenyl-phosphonium 2,3,4,5-tetraphenylcyclopentadienylide, identical to the compound prepared in Experiment 3,vii).

(iii) Triphenylphosphonium 2,3,4-triphenylcyclopentadienylide

a) A preliminary attempt to prepare the ylide was made as follows.- Triphenylphosphine (0.262g., 1m.mole) was added to a solution of 5-bromo-2,3,4-triphenylcyclopentadiene (0.374g., 1m.mole) in nitromethane (15ml.) and the mixture warmed at 60° for 5 min.. On cooling, colourless crystals

were deposited. These were filtered and recrystallised from acetonitrile to give 2,3,4-triphenylcyclopentadiene (0.22g., 75%), m.p. 165°.

b) 5-Bromo-2,3,4-triphenylcyclopentadiene (0.374g., 1m.mole) and triphenylphosphine (0.786g., 3m.moles) were heated together on an oil-bath at 150° for 10 min.. Ether (15ml.) was added to the cooled mass and a yellow precipitate formed. This was filtered off and washed with ether to give triphenyl(2,3,4-triphenylcyclopentadienyl)phosphonium bromide (0.605g., 95%). Perchloric acid (0.2ml., 70%) was added to a solution of the salt in ethanol (4ml.). Colourless crystals separated on addition of ether (15ml.) and these were filtered, washed with ether , and recrystallised from methanol to give triphenyl(2,3,4-triphenylcyclopentadienyl)phosphonium perchlorate (0.47g., 78%) as colourless plates, m.p. 259-261°. (Found: C, 74.7; H, 5.1. $C_{41}H_{32}ClO_4P$ requires C, 75.2; H, 4.9%).

Hydrolysis of the salt.- A solution of 2N sodium hydroxide (2ml.) was added to a suspension of triphenyl-(2,3,4-triphenylcyclopentadienyl)phosphonium perchlorate (0.554g., 1m.mole) in ethanol (20ml.). The mixture was shaken for 10 min. and left for 6 hr.. The yellow precipitate was recrystallised from acetonitrile to give triphenylphosphonium 2,3,4-triphenylcyclopentadienylide (0.34g., 75%) as yellow needles, m.p. 240-243°. (Found: C, 89.1; H, 5.5. $C_{41}H_{31}P$ requires C, 88.8; H, 5.6%).

10. PREPARATION OF TRIPHENYLARSONIUM 2,3,4-TRIPHENYLCYCLOPENTADIENYLIDES

(i) Triphenylarsonium 2,3,4-triphenylcyclopentadienylide

a) A preliminary attempt to prepare the ylide was made as follows.- A solution of 2,3,4-triphenylcyclopentadiene (0.59g., 2m.moles) in methylene chloride (7ml.) was added to a solution of triphenylarsine oxide (0.644g., 2m.moles)(heated in an oven at 140° for 3 hr. before use) in acetic anhydride (15ml.) and the stirred mixture was warmed on a water-bath at 35° for 24 hr.. The solution was poured into water (50ml.), left for 6 hr., and then extracted with methylene chloride. After the extract had been dried (Na_2SO_4) and the solvent removed unchanged 2,3,4-triphenylcyclopentadiene was recovered.

b) Phosphorus pentoxide (1.0g.) was added to a solution of 2,3,4-triphenylcyclopentadiene (2.06g., 7m.moles) and triphenylarsine oxide (2.25g., 7m.moles)(heated in an oven at 140° for 3 hr. before use) in triethylamine (40ml.) and the mixture was heated to reflux for 24 hr.. (After the first 4 hr. more phosphorus pentoxide (0.5g.) was added). Water (100ml.) was added to the reaction mixture and the resultant suspension was extracted with methylene chloride. The extract was washed well with water, dried (Na_2SO_4), and the solvent removed to give an oily residue. Trituration with ether (15ml.) and ethanol (5ml.) gave pale yellow crystals of

triphenylarsonium 2,3,4-triphenylcyclopentadienylide (2.25g., 55%). A sample was recrystallised from acetonitrile as pale yellow needles, m.p. 198-200°(decomp.). (Found: C, 82.1; H, 5.2. $C_{41}H_{31}As$ requires C,82.3; H, 5.2%).

Perchloric acid (0.2ml.,70%) was added to a suspension of the ylide (0.698g., 1m.mole) in ethanol (5ml.) to give an almost colourless solution. Addition of ether precipitated pale yellow crystals which were filtered and recrystallised from a mixture of n-propanol and acetonitrile, with ether added to initiate crystallisation, to give triphenyl(2,3,4-triphenylcyclopentadienyl)arsonium perchlorate as pale yellow needles, m.p. 225-226°(decomp.). (Found: C, 69.9; H, 4.85; Cl, 5.4. $C_{41}H_{32}ClO_4$ requires C, 70.4; H, 4.6; Cl, 5.2%).

(ii) Triphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylide

Dehydrated triphenylarsine oxide (0.966g., 3m.moles) was added to a solution of 2,3,4-triphenylcyclopentadiene (0.882g., 3m.moles) in acetic anhydride (25ml.) and the mixture was heated to reflux for 10 min.. On cooling lustrous crystals separated from the solution and these were filtered and washed with ethanol to give triphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylide (1.34g., 70%). A sample was recrystallised from a mixture of nitromethane and benzene as

yellow prisms, m.p. 249-252°(decomp.). (Found: C, 79.9; H, 5.15. $C_{43}H_{33}OAs$ requires C, 80.6; H, 5.2%).

Perchloric acid (0.2ml., 70%) was added to a suspension of the ylide (0.37g., 0.5m.mole) in acetonitrile (5ml.) and the solution was warmed for 1 min.. Addition of ether (15ml.) caused yellow crystals to precipitate which were filtered to give triphenyl(5-acetyl-2,3,4-triphenylcyclopentadienyl)arsonium perchlorate (0.33g.,95%). A sample was recrystallised from ethanol as yellow plates, m.p.224-226° (decomp.). (Found: C, 69.4; H, 4.5. $C_{43}H_{34}ClO_5As$ requires C, 69.7; H, 4.5%).

11. REACTIONS OF 2,3,4-TRIPHENYLCYCLOPENTADIENYLIDES

(i) Reaction of 2,3,4-triphenylcyclopentadienyl 'onium salts with p-dimethylaminobenzaldehyde

General procedure.- A mixture of the perchlorate (1m.mole), p-dimethylaminobenzaldehyde (1.2m.moles), and acetic anhydride (20ml.) was boiled under reflux for 20 min.. An intensely coloured solution was obtained in each case. The work-up varied slightly from case to case and is given individually.

a) N-(2,3,4-Triphenylcyclopentadienyl)pyridinium perchlorate.- Ether (15ml.) was added to the cooled solution and small crystals separated. Filtration and recrystallisation from acetonitrile, with ether added to initiate crystallisation,

afforded N-(5-p-dimethylaminobenzylidene-2,3,4-triphenylcyclopentadienyl)pyridinium perchlorate (0.35g., 58%), as deep maroon needles, m.p. 170-173°(decomp.). (Found: C, 72.2; H, 5.3. $C_{37}H_{31}N_2ClO_4$ requires C, 73.7; H, 5.15%).

b) Triphenyl(2,3,4-triphenylcyclopentadienyl)phosphonium perchlorate.- The volume of the acetic anhydride was reduced (ca. 5ml.) and ether (15ml.) was added. The dark coloured powder was filtered to give triphenyl(5-p-dimethylaminobenzylidene-2,3,4-triphenylcyclopentadienyl)phosphonium perchlorate (0.45g., 65%). A sample was recrystallised from acetonitrile and ether as dark red-brown needles, m.p. 173° (decomp.). (Found: C, 76.45; H, 5.2; N, 1.6. $C_{50}H_{41}NClO_4P$ requires C, 76.2; H, 5.2; N, 1.8%).

c) Triphenyl(2,3,4-triphenylcyclopentadienyl)arsonium perchlorate.- Ether (15ml.) was added to the cooled solution and a dark precipitate collected. This was filtered, washed with ether, and recrystallised from acetonitrile and ether to give triphenyl(5-p-dimethylaminobenzylidene-2,3,4-triphenylcyclopentadienyl)arsonium perchlorate as dark red-brown needles, m.p. 160-163°(decomp.). (Found: C, 71.0; H, 4.9; N, 2.0. $C_{50}H_{41}NClO_4As$ requires C, 72.7; H, 4.95; N, 1.7%)

(ii) Triphenylarsonium 2,3,4-triphenylcyclopentadienylide

a) Attempted hydrolysis.- The ylide (0.537g., 1m.mole) was added to a solution of sodium hydroxide (1g.) in ethanol

(25ml.) and the suspension was heated to reflux for 18 hr.. Water (50ml.) was added to the mixture which was then extracted with chloroform. Removal of the solvent from the dried (Na_2SO_4) solution gave an oily residue which crystallised as unchanged arsonium ylide (0.50g.) on addition of ether (10ml.).

b) Benzaldehyde.- A mixture of triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.537g., 1m.mole) and freshly distilled benzaldehyde (0.106g., 1m.mole) in carbon tetrachloride (25ml.) was boiled for 18 hr., with the addition of a further quantity of benzaldehyde (0.053g., 0.5m.mole) after the first hour. After evaporation of the solvent the residue was chromatographed on an alumina column prepared with light petroleum. Elution with a (2:1) mixture of light petroleum and benzene brought off a brown band which gave a red-brown solution. Removal of the solvent gave 1,2,3,6-tetraphenylfulvene (0.152g., 35%). A sample was recrystallised from nitromethane as pale red-brown needles, m.p. 175°. (Found: C, 94.4; H, 5.9. $C_{30}H_{22}$ requires C, 94.3; H, 5.8%). A pale yellow band was eluted with methanol and this gave, on work-up with boiling water, triphenylarsine oxide (0.17g.,52%).

c) p-Nitrobenzaldehyde.- A mixture of p-nitrobenzaldehyde (0.15g., 1m.mole) and triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.537g., 1m.mole) in carbon tetrachloride (25ml.) was treated in an identical manner to that described

for the analogous reaction of the tetraphenylcyclopentadienylide (Experiment 6,i,c). The work-up gave triphenylarsine oxide (0.195g., 60%) and a brown solid which was 6-p-nitrophenyl-1,2,3-triphenylfulvene (0.385g., 90%). A sample recrystallised from nitromethane as brown needles and had m.p. 163-165°. (Found: C, 84.3; H, 5.0; N, 3.2. $C_{30}H_{21}NO_2$ requires C, 84.2; H, 4.9; N, 3.3%).

d) Nitrosobenzene.- Triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.537g., 1m.mole) was subjected to the same procedure as described in Experiment 6,i,d). Chromatography of the reaction mixture gave triphenylarsine (0.078g., 30%) and N-phenyl 2,3,4-triphenylcyclopentadienone ketoxime (0.068g., 17%), identical to the compound prepared in Experiment 5, iv).

e) Formylation.- A suspension of triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.538g., 1m.mole) in dimethylformamide (5ml.) was treated with phosphorus oxychloride (0.15ml., ca.2m.moles) and the yellow mixture became clear. After it had been warmed at 60° for 5 min. a 2N solution of sodium hydroxide (5ml.) was added and the mixture quenched with water (50ml.). This was extracted with benzene and the benzene solution was washed well with water and dried (Na_2SO_4). Evaporation of the solvemt and addition of ether (15ml.) to the residue gave triphenylarsonium 5-formyl-2,3,4-

triphenylcyclopentadienylide (0.39g., 63%). A sample was recrystallised from acetonitrile as yellow needles, m.p. 210-212°(decomp.). (Found: C, 81.5; H, 5.2. $C_{42}H_{31}OAs$ requires C, 80.5; H, 5.0%).

Perchloric acid (0.1ml., 70%) was added to a solution of the formylated ylide (0.283g., 0.5m.mole) in ethanol (5ml.). Addition of ether (15ml.) gave a yellow precipitate which was recrystallised from ethanol to give triphenyl(5-formyl-2,3,4-triphenylcyclopentadienyl)arsonium perchlorate (0.34g., 95%) as pale yellow prisms, m.p. 230-232°. (Found: C, 68.9; H, 4.6. $C_{42}H_{32}ClO_5As$ requires C, 69.0; H, 4.4%).

f) Acetylation.- A solution of triphenylarsonium 2,3,4-triphenylcyclopentadienylide (0.538g., 1m.mole) in acetic anhydride (10ml.) was heated to reflux for 3 min. and then cooled. Lustrous crystals appeared which were filtered (0.43g., 75%) and recrystallised from a mixture of nitromethane and benzene to give triphenylarsonium 5-acetyl-2,3,4-triphenylcyclopentadienylide, identical to the compound prepared in Experiment 10,ii).

(iii) Triphenylphosphonium 2,3,4-triphenylcyclopentadienylide

a) Hydrolysis, aldehydes, and nitrosobenzene.- The ylide was recovered unchanged from attempted hydrolysis, attempted reaction with aldehydes, and attempted reaction with nitrosobenzene. The conditions used were those described for each

corresponding experiment using the arsonium ylide (Experiment 11,ii).

b) Formylation.- A suspension of triphenylphosphonium 2,3,4-triphenylcyclopentadienylide (0.493g., 1m.mole) in dimethylformamide (5ml.) was treated under the same conditions as described in Experiment 11,ii,e) to give triphenylphosphonium 5-formyl-2,3,4-triphenylcyclopentadienylide (0.42g., 80%). A sample was recrystallised from acetonitrile as yellow prisms, m.p. 252-253°(decomp.). (Found: C, 86.7; H, 5.4. $C_{42}H_{31}OP$ requires C, 86.5; H, 5.3%).

Perchloric acid (0.1ml., 70%) was added to a solution of the ylide (0.26g., 0.5m.mole) in ethanol (5ml.) to give a bright yellow solution. Ether (10ml.) was added and yellow crystals separated. These were filtered and recrystallised from ethanol to give triphenyl(5-formyl-2,3,4-triphenylcyclopentadienyl)phosphonium perchlorate (0.25g., 81%) as bright yellow prisms, m.p. 247-249°(decomp.). (Found: C, 73.8; H, 5.0. $C_{42}H_{32}ClO_5P$ requires C, 73.9; H, 4.7%).

c) Acetylation.- A solution of triphenylphosphonium 2,3,4-triphenylcyclopentadienylide (0.493g., 1m.mole) in acetic anhydride (15ml.) was heated to reflux for 3 hr.. The solution was cooled and crystals precipitated. These were filtered and washed with ether. Recrystallisation from nitromethane afforded triphenylphosphonium 5-acetyl-2,3,4-triphenylcyclopentadienylide (0.32g., 60%) as pale yellow

plates, m.p. 286°(decomp.). (Found: C, 86.4; H, 5.55. $C_{43}H_{33}OP$ requires C, 86.5; H, 5.5%).

Perchloric acid was added to a solution of the ylide (0.268g., 0.5m.mole) in ethanol (8ml.). Ether (15ml.) was added to the clear solution to give a precipitate of the salt. Filtration and recrystallisation from n-propanol gave triphenyl(5-acetyl-2,3,4-triphenylcyclopentadienyl)phosphonium perchlorate (0.33g., 95%) as yellow prisms, m.p. 228-230° (decomp.). (Found: C, 73.8; H, 5.0. $C_{43}H_{34}ClO_5P$ requires C, 74.0; H, 4.9%).

(iv) Pyridinium 2,3,4-triphenylcyclopentadienylide

a) Formylation.-

N-(5-Dimethylaminomethylene-2,3,4-triphenylcyclopentadienyl)pyridinium perchlorate. Dimethylthioformamide (0.89g., 10m.moles) was added to a solution of N-(2,3,4-triphenylcyclopentadienyl)pyridinium perchlorate (0.47g., 1m.mole) in acetic anhydride (5ml.) and the mixture was boiled for 5 min.. Addition of ether (15ml.) first of all caused an oil to be precipitated but this crystallised after ca. 15 min.. The bright red crystals were filtered (0.32g., 57%) to give N-(5-dimethylaminomethylene-2,3,4-triphenylcyclopentadienyl)-pyridinium perchlorate.

Hydrolysis of the salt.- A solution of 2N sodium hydroxide (15ml.) was added to a solution of the salt

(0.279g., 0.5m.mole) in dimethylformamide (15ml.) and the mixture was shaken well for 5 min. before extraction with ether. The solution was dried and the solvent removed leaving a dark crystalline residue which gave an orange precipitate on addition of ethanol (5ml.). Recrystallisation from a mixture of benzene and petroleum gave pyridinium 5-formyl-2,3,4-triphenylcyclopentadienylide (0.146g., 67%) as orange-red needles, m.p. 250-252°(decomp.). (Found: C,87.3; H, 5.4. $C_{29}H_{21}NO$ requires C, 87.2; H, 5.3%).

12. MISCELLANEOUS REACTIONS

(i) Reaction between 2,3,4,5-Tetraphenyldiazocyclopentadiene and Tetrahydrothiophene-1,1-dioxide

2,3,4,5-Tetraphenyldiazocyclopentadiene (0.396g., 1m.mole) and tetrahydrothiophene-1,1-dioxide (0.72g., 6m.moles) were mixed together and heated at 135° for 5 min. under an atmosphere of nitrogen. At this temperature nitrogen was evolved profusely from the reaction mixture which became maroon-red in colour. It was cooled, dissolved in a small amount of benzene, and chromatographed on an alumina column prepared with light petroleum. Unreacted diazo compound (0.01g.) was eluted with a mixture of light petroleum and benzene (3:1) and when the ratio of solvents was changed to (1:3) a purple band was eluted. On removal of the solvent

and addition of ethanol (15ml.) black crystals of 2,3,4,5-tetraphenylcyclopentadienone (0.27g., 70%) were obtained. Benzene eluted a brown band which gave a red-brown oil. A similar red-brown oil was obtained on elution with methanol. Both these oils, in ethereal solution, were passed through a gas chromatogram and were shown to have the same retention time as an authentic sample of tetrahydrothiophene-1,1-dioxide. This was appreciably different from the retention time of tetrahydrothiophene-1-oxide.

(i) Reaction between Pyridinium 2,3,4,5-tetraphenylcyclopentadienylide and Triphenylphosphine

A mixture of pyridinium 2,3,4,5-tetraphenylcyclopentadienylide (0.89g., 2m.moles) and triphenylphosphine (1.05g., 4m.moles) was heated on an oil-bath at 210° for 15 min. and the blue solution darkened. Ether (15ml.) was added to the cooled mixture and dark almost black crystals separated. The precipitate (0.52g.) was filtered, washed with ether, and recrystallised from nitromethane to give purple-black prisms of an unidentified substance, m.p. 296-300°. (Found: C, 90.7; H, 5.7; N, 3.6%). Mol. Wt.($CHCl_3$) 575.

13. pK_a DETERMINATIONS[136,82]

Optical density measurements for the pK_a determinations were carried out on a Unicam S.P.800 spectrophotometer. pH determinations were carried out with a Radiometer Copenhagen pH Meter 25 equipped with glass and saturated calomel electrodes. All optical density measurements and pH determinations were recorded at 25°.

95% Ethanol was the solvent used for all solutions of acids, bases, buffers, and ylide perchlorates. The acid solution was 0.1M HCl prepared by adding water (50ml.) and absolute ethanol (950ml.) to concentrated hydrochloric acid (9.3ml.). The base solution was 0.1M KOH prepared by dissolving potassium hydroxide (5.61g.) in water (50ml.) and absolute ethanol (950ml.).

Ten buffer solutions were prepared as previously described in the literature[137] except that the final solvent composition was 95% ethanol-water. The apparent pH of each buffer* was 8.74(9.0), 8.44(8.6), 7.81(8.0), 7.40(7.8), 7.05(7.2), 6.11(4.0), 5.78(3.6), 5.33(3.4), 5.14(3.2), 4.9(3.0). The first five were Tris-HCl buffers (Tris= tris-(hydroxymethyl)aminomethane), and the other five were formic acid - potassium hydroxide buffers.

*(The values in parentheses are the pH values of the same buffers when prepared in aqueous media).

Stock solutions of each ylide perchlorate were prepared by dissolving the salt (ca.4mg.) in 95% ethanol (10ml.). Aliquots (1ml.) of each stock solution were diluted to 10ml. separately with the acidic solution, the basic solution, and the appropriate buffer solution.

The absorbancy of the three solutions was recorded at five wavelengths in the region (260-350mμ) where the ylides absorbed strongly and the conjugate salts were nearly transparent. The pK_a values were calculated as follows.[136]

$$pK_a = pH - \log \frac{B - b}{b - A}$$

where B = absorbancy of the stock aliquot in basic solution, b = absorbancy of the stock aliquot in buffered solution, A = absorbancy of the stock aliquot in acid solution, and pH = pH of the buffer solution used.

The values recorded are the average of the pK_a's determined using at least two different buffers. The pK_a determined using any given buffer solution is the average of the pK_a values determined at five different wavelengths.

Results:

Ylide	pK_a	Ylide	pK_a
(38)	5.3	(49)	<5.3
(39)	7.6	(50)	?
(40)	>7.6	(62)	4.2
(48)	<5.3	(63)	6.6

14. SPECTRA

A. U.V. SPECTRA

i) U.V. Spectra of Tetraphenyl- and Triphenylcyclopentadienylides recorded in a) Ethanol, b) Ethanol + 1% v/v 70% perchloric acid, or as indicated.

(Compounds are numbered as in Part II, p.32).

Compound	λ_{max} (log ϵ) mμ
(38)	(a)288(4.30), (b)268sh*(4.42) 345(3.88)
(39)	(a)291(4.27), (b)245sh(4.31) 347(3.74)
(40)	(Chloroform)253(4.35) 349(4.11)
(15)	(a)240sh(4.82) 335(4.2) 525(3.90), (Benzene)280(5.19) 345(4.38) 596(4.06)
(1)	(a)260(5.30) 337(4.41) 538(3.10), (Benzene)286(5.21) 345(4.20) 595(3.32)
(48)	(Benzene)292(4.44) 328sh(3.85)
(49)	(Benzene)302(4.28) 346sh(3.74)
(50)	(a)294(4.30) 347sh(3.61), (b)252(4.20) 335(3.61)
(62)	(a)286(4.30), (b)263sh(4.2) 340(4.00)
(63)	(a)288(4.35), (b)265(4.31) 335sh(2.30)

*sh denotes shoulder.

(57)	(a)255(3.34) 311(3.40) 530(3.10), (b)232(2.63) 303(2.28) 362(2.01), (Benzene)292(3.50) 320(3.35) 582(3.41)
(66)	(a)268(3.77) 287((3.65) 326(3.49) 447(2.86), (b)253(3.71) 311(3.46) 400sh(2.81) (Benzene)294(3.66) 326sh(3.20) 528(2.98)
(73, X=P)	(a)265(3.45) 325(3.29) 354(3.10)
(73, X=As)	(a)268(3.82) 325(3.15) 354(3.20)
(74, X=P)	(a)285(4.68)
(74, X=As)	(a)287(4.58)

(ii) U.V. Spectra of Fulvenes, Anils, and N-oxides recorded in chloroform.

(41)	275(3.65) 346(3.56)
(42)	273(3.59) 353(3.45)
(69)	258(3.54) 350(3.64)
(70)	273(3.54) 361(3.60)
(44)	256(3.76) 325sh(3.23) 450(2.65)
(72)	261(3.65) 321(3.18) 408(2.77)
(45)	250(3.53) 363(3.45)
(71)	256(3.52) 362(3.52)

(iii) U.V. Spectra of other Compounds

(10)	(Cyclohexane)245(3.61) 282(3.60) 364sh(2.34)
(25)	(Chloroform)345sh(3.62) 317(3.71) 307(2.46) 220(3.82)

(26)	(Ethanol)220(3.82) 265(3.64) 362(3.50), (Ethanol + 1% v/v 70% perchloric acid)228(3.87) 263(3.68) 341(3.56)
(28)	(Ethanol)261(2.91) 268(2.90) 275sh(2.80) 366(3.72), (Ethanol + 1% v/v 70% perchloric acid)223(3.65) 260(2.83) 261(2,91) 273(2.87) 338(3.59)
(30)	(Chloroform)263(3.58) 346(3.51)
(31)	(Chloroform)265(3.63) 349(3.77)
(33)	(Ethanol)250sh(4.42) 373(4.32), (Ethanol + 1% v/v 1M KOH solution)258(4.39) 382(3.98)

B. N.M.R. SPECTRA

Chemical shifts (τ) are given in p.p.m. relative to tetramethylsilane as internal standard with relative intensities in parentheses.

(Compounds are numbered as in Part II, p.32)

(10)	2.96m(30)	4.80s(1)
(50)	2.85m(25)	7.24s(3)
(54)	2.90m	3.51d 4.40d 6.20s J = 2
(56)	1.2↔2.8m(20)	5.61s(2)
(61)	2.0↔3.2m(30)	5.88s(2)
(64)	2.2↔3.3m(30)	5.64s(2)
(66)	0.50s(1)	1.3↔3.3m(20)

(73, X=P)	2.1↔3.4m(30)	8.21s(3)
(73, X=As)	2.2↔3.5m(30)	8.18s(3)
(74, X=P)	2.1↔3.3m	
(74, X=As)	2.2↔3.4m	

s = singlet, d = doublet, and m = multiplet.

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